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### *The Gibeon shower of meteoritic irons in South-West Africa.*

(With Plates I and II.)

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[Read March 13, 1941.]

THE presence of much native iron in Great Namaqualand was heard of in 1836 by the traveller Sir James E. Alexander,<sup>1</sup> but he himself did not see any of the masses, and the material he acquired consisted only of small fragments that had been detached by the natives for pointing their weapons. An approximate chemical analysis of this material, made by Sir John Herschel,<sup>2</sup> proved it to be meteoritic. A fragment weighing 2 grams which Alexander presented to the Geological Society of London in 1838 was transferred to the British Museum collection of meteorites in 1911. This appears to be all of his material that has been preserved.

Various other vague reports and travellers' tales have mentioned the presence of large masses of iron beyond the old mission station of Bethany, between there and Beersheba, and on the east side of the Great Fish River. A critical summary of these accounts was given by Sir Lazarus Fletcher in this magazine.<sup>3</sup> Further historical details are

<sup>1</sup> J. E. Alexander, An expedition of discovery into the interior of Africa through the hitherto undescribed countries of the Great Namaquas, Boschmans, and Hill Damaras. London, 1838, vol. 1, p. 145, vol. 2, p. 272. Journ. Roy. Geogr. Soc., 1938, vol. 8, p. 24.

<sup>2</sup> J. F. W. Herschel, Notice of a chemical examination of a specimen of native iron, from the east bank of the Great Fish River, in South Africa. Phil. Mag. London, 1939, ser. 3, vol. 14, pp. 32-34. (Reprinted from the appendix of Alexander's book.)

<sup>3</sup> L. Fletcher, On various masses of meteoric iron reported to have been found

given in E. Cohen's 'Meteoritenkunde' (Stuttgart, 1905, Heft. 3, pp. 324-342), and in G. T. Prior's British Museum 'Catalogue of Meteorites' (1923 and appendices 1927, 1940).

The first large block actually recovered was one of 178 lb. (81 kg.), which was transported from the Lion River (map, fig. 1) via Cape Town and London to Amherst College, Massachusetts, where it was described by C. U. Shepard<sup>1</sup> in 1853. The collector, John Gibbs, stated that it was found on a clay plain near the Lion River in the close vicinity to one or more masses too heavy for transport. [But there appears to have been no later mention of these other masses.]

A second large mass of 511 lb. (232 kg.), referred to by Fletcher as 'the Wild mass', was sent to the South African Museum in Cape Town by John Wild in 1857. This was described in 1900 under the name 'Bethany' by E. Cohen,<sup>2</sup> who stated that it had long been known to the missionaries at Bethany, and after being brought as far south as the Orange river it was later transported to Cape Town. The label with the specimen in the Cape Town Museum (which I visited in 1929) states: 'Said to have been found at Bethany, Great Namaqualand, and to have been brought down to the Orange River by a trader. . . .'

The first record from the Gibeon region was a block of 178 kg. found at Mukerop (Mukorob, Mukorub) farm in 1899 and described by A. Brezina and E. Cohen<sup>3</sup> and independently by F. Berwerth<sup>4</sup> in 1902. This was followed by a mass of 404 kg. from Goamus farm described by F. Rinne<sup>5</sup> in 1910. Between these two dates several large meteoritic irons from the Gibeon district were exported to Germany and deposited in Great Namaqualand and the adjacent region. *Min. Mag.*, 1904, vol. 14, pp. 28-36.

<sup>1</sup> C. U. Shepard, Notice of meteoric iron near Lion river, Great Namaqualand, South Africa. *Amer. Journ. Sci.*, 1853, ser. 2, vol. 15, pp. 1-4, 1 fig.

<sup>2</sup> E. Cohen, The meteoric iron from Bethany, Great Namaqualand. *Ann. South African Museum*, 1900, vol. 2, pp. 21-29, 4 pls. *Das Meteoreisen von Bethanien, Gross-Namaland, West-Südafrika. Mitt. Naturwiss. Ver. Neu-Vorpommern und Rügen*, Berlin, 1901, vol. 32 (for 1900), pp. 12-25, 3 pls.

<sup>3</sup> A. Brezina and E. Cohen, Ueber ein Meteoreisen von Mukerop, Bezirk Gibeon, Grossnamaland. *Jahresh. Ver. Naturk. Württemberg*, 1902, vol. 58, pp. 292-302, 1 pl.

<sup>4</sup> F. Berwerth, Über das neue Meteoreisen von Mukerop. *Anzeiger Akad. Wiss. Wien, Math.-naturwiss. Cl.*, 1902, vol. 39, pp. 46-49. *Der Meteoreisenzwilling von Mukerop, Bezirk Gibeon, Deutsch-Südwest-Afrika. Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Cl.*, 1902, Abt. I, vol. 111, pp. 646-666, 1 pl., 2 text-figs.

<sup>5</sup> F. Rinne, Ein Meteoreisen mit Oktaeder- und Würfelbau (Tessera-Oktaedrit). *Neues Jahrb. Min.*, 1910, vol. 1, pp. 115-117, 2 pls.

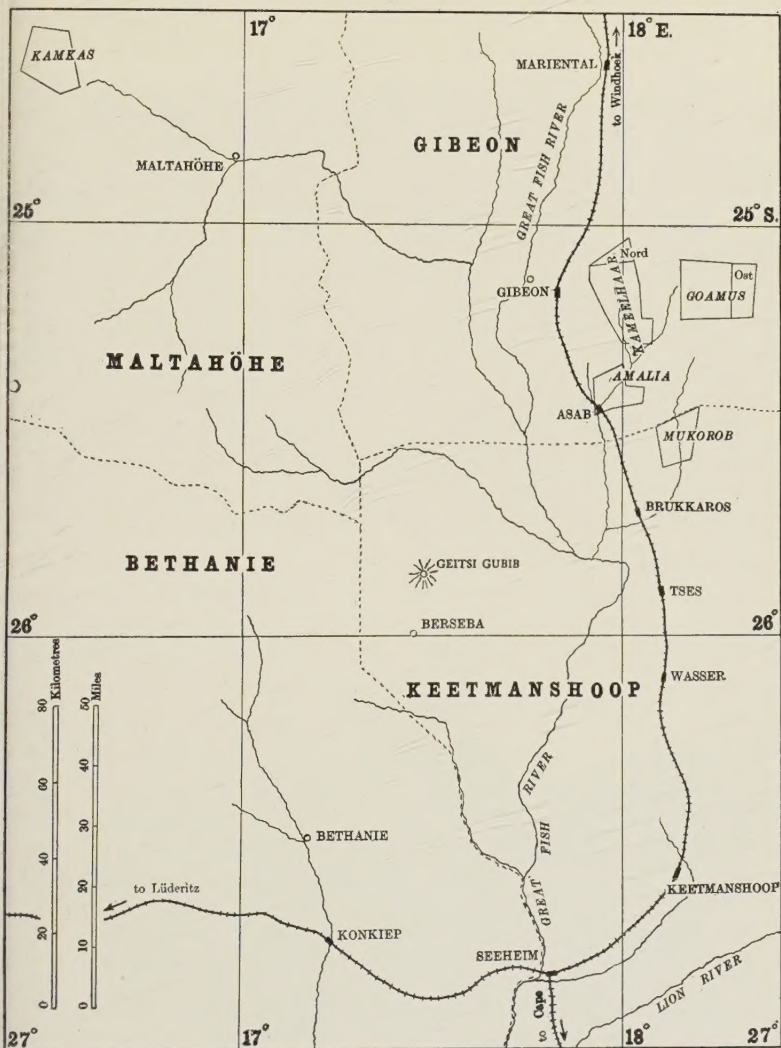


FIG. 1. Sketch-map of meteorite localities in Great Namaqualand, South-West Africa. Adapted from the Farm Area maps 1896 and 1930 (scale of originals 1 : 800,000).

The Lion (= Xamob = Kamob = Chamob = Kamop = Löwen) River joins the Great Fish (= Fish = Oup = Boradaile Aub = Grosser Fisch) River at  $27^{\circ} 10' S.$ , and the latter joins the Orange River at  $28^{\circ} 10' S.$

in German museums. W. Schrauf<sup>1</sup> in 1912 estimated the total amount at 2312 kg.

P. Range,<sup>2</sup> the former Government Geologist of South-West Africa, tells that in 1907 he saw seven large blocks, with a total weight of 28 cwt., set up outside the farm-house of Goamus. These had been collected from the neighbouring farms Amalia and Kameelhaar. They were sold by the farmer and were no doubt the ones shipped to Germany. Several other masses were mentioned by Range, and in 1911 he was instructed by the Government to collect together such masses as were still available. Further masses were found over an area of 200 sq. km. on the Amalia and Kameelhaar farms to the south-east and east of Gibeon. The result was that during 1911-12 thirty-seven masses weighing from 134 to 600 kg. and totalling 12,613 kg. were taken to Windhoek. He estimated that by that time (1912) fifty-one masses with a total weight of over 15 tons had been removed from the Gibeon district.

In 1930 W. Edlinger, a German mining engineer, obtained from Kameelhaar farm three masses weighing 195.2, 188.9, and 132.17 kg., although the property in meteorites was vested in the State and their export prohibited. Two of these were sold to America and cut into slices, and the third was described and figured by V. Zsivny,<sup>3</sup> it having been offered to but declined by the Hungarian National Museum.

During my visit to South-West Africa with the excursion of the International Geological Congress in 1929 I saw the pile of meteorites collected by Dr. Range in the Public Garden at Windhoek.<sup>4</sup> The specimen to which I am pointing with the walking-stick in fig. 2 was generously presented by the Administration of South-West Africa, through Mr. L. G. Ray, then Chief Inspector of Mines, to the British Museum,

<sup>1</sup> W. Schrauf, Die grossen Eisenmeteoriten aus Deutsch-Südwestafrika. Ber. Senckenberg. Naturfor. Gesell. Frankfurt am Main, 1912, vol. 43, pp. 214-221, 2 figs.

<sup>2</sup> P. Range, Geologie des deutschen Namalandes. Beitr. Geol. Erforsch. Deut. Schutzgeb. Berlin, 1912, Heft 2, pp. 67-70. Meteoriten aus Deutsch-Südwestafrika. Mitt. Deut. Schutzgeb. Berlin, 1913, vol. 26, pp. 341-343, 2 figs. (sketch-map).

<sup>3</sup> V. Zsivny, Egy délnyugatafrikai meteorvasról. [A South-West African iron meteorite.] Pótfüzetek a Természettudományi Közlönyhöz, Budapest, 1932, vol. 64, pp. 84-87, 2 figs. [M.A. 5-155.]

<sup>4</sup> L. J. Spencer, Meteoric irons from South-West Africa. Nat. Hist. Mag. British Museum, 1930, vol. 2, pp. 240-246, 5 figs. [M.A. 4-422.] This popular article was rewritten by Mary Proctor in Everyman's Astronomy, London, 1939, chap. XIII, pp. 189-197, 2 pls. [M.A. 8-55.]

in which collection none of the larger masses from this fall was previously represented. It weighs 299 lb. (136 kg.) and was selected as an example



FIG. 2. Pile of meteoritic irons (some thirty, weighing about 10 tons) in the Public Garden at Windhoek. (Photo. by Prof. W. T. Gordon, September 1929.)

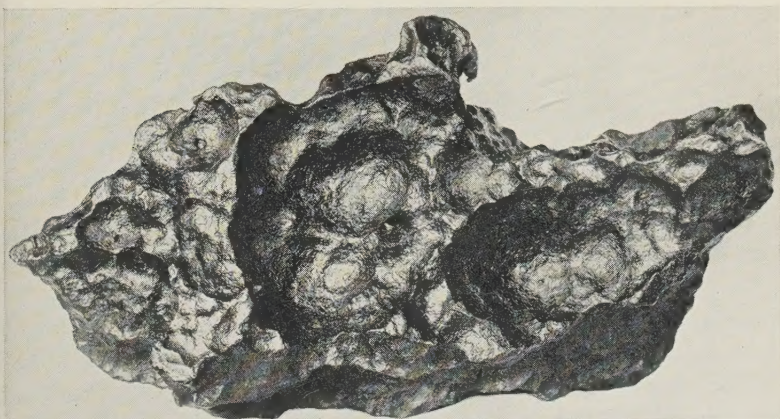


FIG. 3. Meteoritic iron from near Gibeon. 299 lb. (136 kg.),  $26 \times 13$  inches. (British Museum no. 1930,422.)  $\times \frac{1}{7}$ .

of prominent surface pitting (fig. 3). During my visit I was also able to obtain from Dr. Range some further information about these meteorites. Unfortunately I was not able to break my journey at Gibeon, but was told by the station-master there and by the sergeant of police that several large masses were still lying on the Kameelhaar farm 12 miles

east of Gibeon. A small meteorite weighing 195 grams (fig. 4) was given to me for the British Museum collection by the station-master, Mr. P. James.

This is the smallest individual mass of the Gibeon irons that has been recorded. No doubt other small masses have been found and

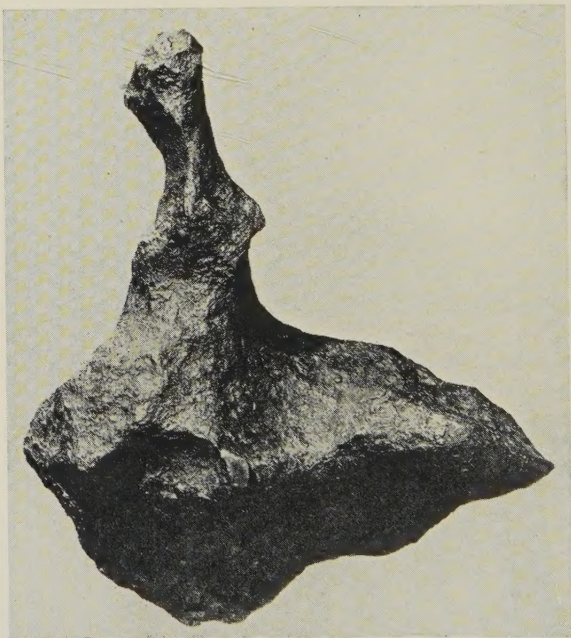


FIG. 4. Meteoritic iron from near Gibeon. 195 grams.  
(British Museum no. 1929,1563.) Actual size.

remain to be found. Dr. Range remarked that they are difficult to find, being embedded in the surface limestone (Kalahari Kalk). The largest mass of this fall is one of 1431 lb. (650 kg.) which was presented by the Administration of South-West Africa to the South African Museum at Cape Town. (This was presumably from the collection of 37 masses at Windhoek, but amongst these the largest weight mentioned by Dr. Range was 600 kg.)

It is therefore evident that the centre of this large shower of iron meteorites was in the Gibeon district. The iron had been used by the natives, and it is also evident that some of the large masses had been transported. Curiously, Sir L. Fletcher (1904, loc. cit., p. 34) suggested

that the first Mukerop mass found in 1899 had been transported, while the Lion River mass, having been said to be associated with other masses, he considered to have been found in place. But transportation towards centres of civilization is more probable than in the reverse direction. The 'Bethany' mass described by E. Cohen had evidently been transported, first to Bethany and then to the Orange River before being finally taken to Cape Town; and there is no evidence that any large mass has been found in place in the Bethany district.

The name 'Bethany' for this meteoritic fall was suggested by E. Cohen in 1900 to replace the indefinite designations 'Great Namaqualand' and 'Great Fish River'. This change was favoured by Sir L. Fletcher and has since been followed in meteorite catalogues. 'Gibeon' would seem to be a better term. The several masses concerned have in common a fine octahedral structure and a nickel content of about 8 % (p. 34).

The farm names Amalia, Goamus, Kameelhaar, and Mukerop are without significance as applied to the separate meteorites. The masses from the different areas have been mixed up: as mentioned above, they have been transported from one farm area to another, and at Windhoek they were all placed together in one huge pile (fig. 2). From this pile a few specimens have from time to time been distributed to various museums. The country is divided into a network of farm areas, and some of the meteorites quite likely came from farms lying between those named above; e.g. Noronaub, Korra Korrabes, Grundorner, Gaus, &c. These farm areas are of considerable size: Kameelhaar is almost twenty miles long and Goamus more than a hundred square miles. In this stony and semi-desert region grazing is very sparse, but after rain the result is surprising and a fairyland of flowers springs up as if by magic. The average rainfall at Gibeon is 6.36 inches, but in different years (1921-26) it varied from 1.99 to 16.39 inches. The rivers on the map (fig. 1) are dry rivers showing as sandy tracks, except when in flood.

The distribution of these masses over an area of several hundred square miles and the fact that they are all of considerable size suggest that the shower was a swarm of meteorites, rather than a single mass broken up in the earth's atmosphere as is the case with showers of stones. Again, the distribution and relative sizes of the masses is here quite different from that of meteoritic iron found around a meteorite crater, where a single large mass of iron was shattered by the gaseous explosion, yielding a preponderance of smaller distorted fragments.

There is in this region a remarkable topographical feature which may

possibly have some connexion with these meteorites. This is the large crater of the Geitsi Gubib or Groot Bukaros mountain, which has been described in some detail by A. W. Rogers.<sup>1</sup> The mountain has a height of 5200 feet above sea-level and 1800 feet above the plateau, and it is a prominent feature seen from the railway to Gibeon. (Unfortunately this is all that I saw of it.) The crater is  $1\frac{1}{3}$  miles across and the flat bottom is 1500 feet below the highest point of the rim. This is considerably larger than the Arizona meteorite crater ( $\frac{3}{4}$  mile in diameter and 570 feet deep). The material of the mountain is a fine breccia (fragments usually less than an inch across) of sedimentary rocks—hard shales, jaspery rocks, sandstones, &c.—with some quartz-gabbro and fragments of felspar, but no volcanic material. There are no volcanic rocks in the neighbourhood, but between here and Gibeon there are many kimberlite pipes (without diamonds). Rogers describes it as an explosion-pipe penetrating shales and sandstones of the Fish River series; and he accounts for the crater by the weathering of softer material inside a ring of silicified rocks, or by a ring fault. He remarks on the close similarity to the Arizona crater as described by G. K. Gilbert (1896), who favoured the explosion volcanic theory and rejected the meteoritic theory of its origin (now amply proven). There is, however, one important difference between these two craters. The thick beds of breccia at Geitsi Gubib dip inwards, while at the Arizona crater the beds dip outwards.

Another remarkable feature is presented in the situation of Geitsi Gubib. Ignoring for the moment the probability that the meteorites of Lion River, Bethany, and Kamkas (p. 32) were transported masses from the Gibeon district, it will be seen from the map (fig. 1) that this large crater lies near the centre of a ring of meteorite finds. But this cannot be put forward seriously in support of a meteoritic origin of the crater. Still another coincidence is the presence of kimberlite pipes between Geitsi Gubib and Gibeon, with a cluster close to where meteorites have been found, as shown on Range's maps (1912 and 1913, loc. cit.). But the idea that there can be any connexion between meteorites, kimberlite pipes, and diamonds is really too fantastic.<sup>2</sup>

Two specimens of meteoritic iron from this region were presented through Mr. L. G. Ray to the British Museum collection in 1940 by

<sup>1</sup> A. W. Rogers, Geitsi Gubib, an old volcano. *Trans. Roy. Soc. South Africa*, 1915, vol. 5, pp. 247–258, with sketch-map and section. A. L. du Toit, *The geology of South Africa*, 1939, p. 392.

<sup>2</sup> H. Helberger, Kann der Diamant kosmogenetischen Ursprungs sein? *Zeits. Prakt. Geol.*, 1934, vol. 42, pp. 124–125. [M.A. 6–8.]

Mr. E. Zelle, meteorologist to the Administration of South-West Africa. These came from the Kameelhaar and Kamkas farms, but unfortunately details of the finding and weights of the masses from which they were cut are not yet available.

#### KAMEELHAAR FARM, GIBEON.

As received, this piece weighed 1453 grams. After levelling and polishing two of the cut surfaces and cutting off a fragment for chemical analysis the weight is now 1439 grams (B.M. 1941,1). A portion of the larger ( $14 \times 6$  cm.) polished and etched surface is shown, actual size, in pl. I, fig. 8. The natural surface at the back of the specimen shows a series of shallow pits. The section shows one large ( $3 \times 2$  cm.) and several smaller troilite nodules. This specimen is of special interest in consisting of two crystal individuals, as shown by the different orientation of the Widmanstetter figures on two portions of the section. This is well shown by the enlarged ( $\times 3$ ) photograph reproduced in pl. II, fig. 11. The junction is marked by a kamacite band which, along its course, is approximately parallel to kamacite bands in one or other of the two crystals. The kamacite bands are about  $\frac{1}{3}$  mm. in width, corresponding to a fine octahedrite; but in some parts of the section they are much finer and more closely packed together. Narrow bands of taenite bordering the kamacite shine up brightly at certain inclinations of the specimen in the light. Plessite areas are rather smaller in one crystal than in the other. In the crystal on the right (larger portion in pl. II) the kamacite bands are somewhat irregular and confused, and they show more than the four directions required by the Widmanstetter structure parallel to the faces of the octahedron. Prominent amongst the extra bands are a few longer bands (vertical in the picture, pl. II). At an angle of  $85^\circ$  to these is a series of less distinct bands, seen to the left near the contact of the two crystals. A third extra direction is represented by a short band forming a hook at  $10^\circ$  at the top of the long vertical band. These three sets of bands are similar to the subordinate system of longer (up to 3 cm.) bands parallel to the faces of the cube which were described by F. Rinne<sup>1</sup> in the 404 kg. Goamus mass. For this new type of structure he suggested the term 'tessera-octahedrite'. O. C. Farrington<sup>2</sup> modified this to 'tesselated octahedrite'.

<sup>1</sup> F. Rinne, 1910, loc. cit. In this case, as the section plane was parallel to a cube face, there are actually only four directions of the lines: one set at right angles for the octahedron and another set also at right angles for the cube, the two sets being at  $45^\circ$  to one another.

<sup>2</sup> O. C. Farrington, *Meteorites*. Chicago, 1915, p. 95.

Still better would be cubo-octahedrite. Of the seven directions shown by these Widmanstetter figures four belong to the octahedron and three to the cube.

The crystal on the left (pl. II) shows only the four directions as required by the octahedral structure. The essential angles between these four directions are given in fig. 5A. But in addition to these angles there are several others at which the different directions may intersect.<sup>1</sup> Some of the several polygons that may so result are represented in the upper part of fig. 5. Similar shapes will be seen in the crystal on the left in pl. II. The essential angles of the seven directions in the other crystal (right-hand side of pl. II) are shown in fig. 5B.

The determination of the orientation of the section plane from the directions of the lines of the Widmanstetter figures involves complex formulae with tedious calculations<sup>2</sup> or a tangled graphical method.<sup>3</sup> These I have not attempted, but have obtained an approximate result by trial and error with the Hutchinson stereographic net.<sup>4</sup>

On the stereographic projection (fig. 6) are drawn the great circles at  $90^\circ$  from the poles of the octahedron and cube faces. They represent the intersections on the sphere of planes through its centre parallel to these faces. The section plane is also represented by a great circle; and the arc distances between its points of intersection with the several zone circles give the plane angles between the intersection of crystal faces on the section plane. This is made clearer by models. Disks of cardboard parallel to the faces of the octahedron and passing through

<sup>1</sup>  $73^\circ = 36^\circ + 37^\circ$ ,  $77^\circ = 36^\circ + 41^\circ$ ,  $103^\circ = 37^\circ + 66^\circ$ ,  $107^\circ = 41^\circ + 66^\circ$ ,  $114^\circ = 180^\circ - 66^\circ$ ,  $139^\circ = 180^\circ - 41^\circ$ ,  $143^\circ = 180^\circ - 37^\circ$ ,  $144^\circ = 180^\circ - 36^\circ$ .

<sup>2</sup> A. Brezina, *Meteoreisenstudien II. Über die Orientirung der Schnittflächen an Eisenmeteoriten mittelst der Widmannstädten'schen Figuren*. Denkschr. Math.-naturwiss. Cl. Akad. Wiss. Wien, 1881, vol. 44, pp. 121-158, 5 pls., 11 text-figs.

N. T. Belaiew, *The inner structure of the crystal grain as revealed by meteorites and Widmanstätten figures*. Journ. Inst. Metals, London, 1923, vol. 29, pp. 379-403, 1 pl., 18 text-figs. *Crystallisation of metals*. London, 1923, pp. 72-78. [M.A. 2-87, 5-483.]

J. Leonhardt, *Die morphologischen und strukturellen Verhältnisse der Meteor-eisen im Zusammenhang mit ihrem Entwicklungsgang*. Fortschr. Min. Krist. Petr., 1927, vol. 12, pp. 52-55; Neues Jahrb. Min., Abt. A, 1928, vol. 58, pp. 153-212, 2 pls., 9 text-figs. (pp. 179-201: Orientierungsmethoden und ihre Anwendung zur Untersuchung geometrischer und kristallographischer Zusammenhänge). [M.A. 3-533, 4-122.]

<sup>3</sup> A. Himmelbauer, *Orientierung von Schnittflächen an Meteor-eisen*. Min. Petr. Mitt. (Tschermak), 1909, vol. 28, pp. 153-166, 8 figs.

<sup>4</sup> A. Hutchinson, *Min. Mag.*, 1908, vol. 15, p. 100, pls. iv, iva.

a common centre are built up of  $60^\circ$  sectors, the disks being of different colours for the two individuals and for the section plane.

The very few known examples of slices of meteorites showing two large crystal individuals in contact have been described as spinel-twins; and it was at first assumed that here we also have a spinel-twin.

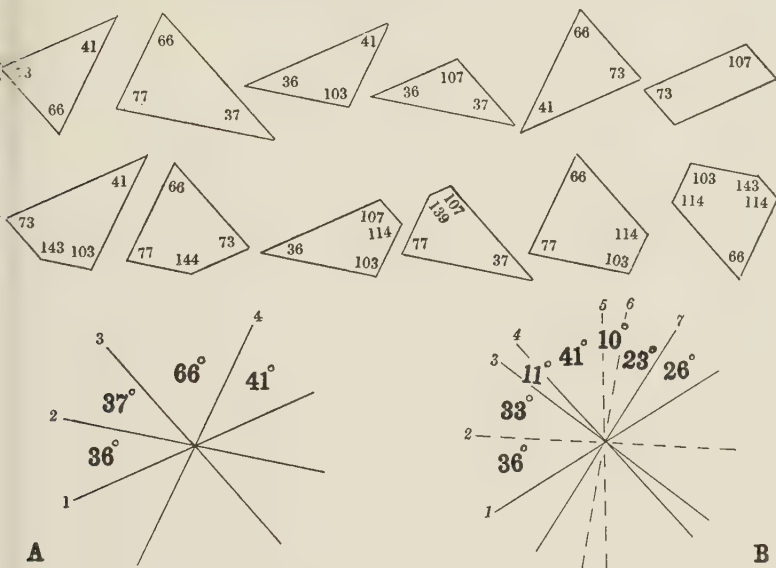


FIG. 5A. Direction of the lines of the Widmanstetter figures in one crystal individual (left-hand side of pl. II).

FIG. 5B. Same for the other crystal individual (right-hand side of pl. II). Barred lines for the direction of cube faces.

The polygons in the upper part of the figure show the various shapes given by the angles in fig. 5A and seen on the left in pl. II.

The section plane as drawn in fig. 6 shows a good agreement in the angles for the portion *A* and a tolerable agreement for the portion *B*. The following angles were measured: I, on the photograph<sup>1</sup> (pl. II) and given in fig. 5; II, on the stereographic projection (fig. 6); *A* for the crystal-individual on the left and *B* for that on the right; *o* for octahedral faces and *a* for cube faces;  $\bar{o}$  as twin-plane.

|   |    |     |     |     | 1-2( $\bar{o}o$ ). | 2-3( $oo$ ). | 3-4( $oo$ ). | 4-1( $o\bar{o}$ ). |            |
|---|----|-----|-----|-----|--------------------|--------------|--------------|--------------------|------------|
| A | I  | ... | ... | ... | ...                | 36°          | 37°          | 66°                | 41° = 180° |
|   | II | ... | ... | ... | ...                | 32           | 39           | 68                 | 41 = 180   |

<sup>1</sup> The photographic plate was inclined at about  $5^\circ$  to the surface of the section, but this makes no appreciable difference in the angles.



Large-scale spinel-twinning in meteoritic iron was first described in the Mukerop mass of 178 kg. by A. Brezina and E. Cohen and independently by F. Berwerth in 1902. Berwerth (*loc. cit.*, 1902, p. 663) also mentioned and figured a spinel-twin in a small slice from the 'Bethany' mass of 232 kg. The twin-law in these two examples was confirmed by a graphical method by A. Himmelbauer in 1909, and he added (*loc. cit.*, p. 157) a third example in the siderite (also a fine octahedrite) of Laurens County (South Carolina, found 1857). Spinel-twins of this gigantic size are surely unique in any material.

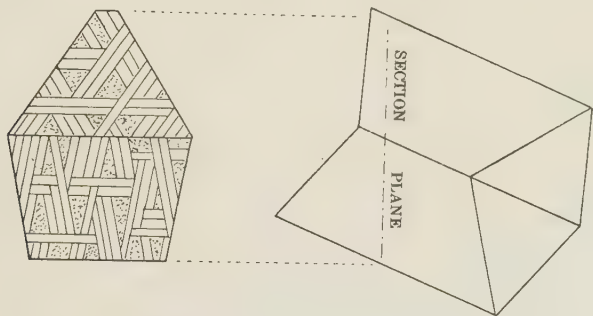


Fig. 7. Widmanstetter figures on a section of a spinel-twin.

Small-scale twinning on (111) had been previously described by G. Linck.<sup>1</sup> On a specimen of the Toluca siderite two small cleavages at  $38^{\circ} 58'$  were interpreted as cube planes each twinned on different octahedral planes of a third crystal. This multiple twinning he believed to account for the oriented sheen sometimes seen on kamacite; and he further suggested that the Widmanstetter structure itself was due to polysynthetic twinning on four octahedral planes. Slip-band lamellar twinning on (211), as shown by Neumann lines in kamacite, is of frequent occurrence in siderites.<sup>2</sup>

A diagrammatic representation of Widmanstetter figures on a section of a spinel-twin is given in fig. 7. Here, as the section plane and the twin-plane are both perpendicular to the same dodecahedral plane of symmetry (for convenience in drawing), there are only three directions of the lines in each portion of the twin. The section plane is inclined at  $5^{\circ}$  to an octahedral plane of one individual of the twin and at  $11^{\circ}$

<sup>1</sup> G. Linck, Ueber das Krystallgefüge des Meteoreisens. *Ann. Naturhist. Hofmus. Wien*, 1893, vol. 8, pp. 113-117, 1 fig.

<sup>2</sup> L. J. Spencer, *Min. Mag.*, 1930, vol. 22, p. 276; 1931, vol. 22, p. 493; 1932, vol. 23, p. 39; 1933, vol. 23, pp. 331, 388; 1935, vol. 24, p. 15.

to a cube face of the other individual. I give this figure because the much-copied figures of Tschermak,<sup>1</sup> showing section planes in four directions on octahedra, represent the sections completely filled by kamacite bars without any intervening plessite areas.

Meteorite specimens of the octahedrite and hexahedrite types usually seem to consist of a single crystal, there being a continuity of the structure throughout the whole mass whatever may be its size. The only examples that I know of where the mass consists of more than one large crystal are the few mentioned above. In other cases the mass may consist of an aggregate of small crystals, sometimes still showing remnants of a previous octahedral structure, as in Murnpeowie and Kamkas. It seems probable that the granular structure of ataxites may be due to the same heat-treatment with complete obliteration of the original structure.

#### KAMKAS FARM, MALTAHÖHE.

The only available information about the finding of this mass of meteoritic iron is given in Mr. E. Zelle's letter of July 17, 1940: 'It was found on the farm Kamkas on the hard ledge of a small flat river in the Fish River series [Nama System = Cambrian?], about 3 miles from the farm-house. At my request it was taken to a shop in Malta-höhe, where it was loaded on to a farmer's motor-car and brought to Windhoek.' It is thus evidently a large mass, but no mention is made of its weight.

The slice as received weighed 819 grams; after polishing and sawing off a fragment for chemical analysis the weight is now 810 grams (B.M. 1941,2). The polished and etched surface measures  $10 \times 5\frac{1}{2}$  cm. This surface is dull and granulated, but at certain inclinations of the light it shows indistinctly a fine octahedral structure (pl. 1, fig. 9). The enlarged ( $\times 3$ ) photograph (fig. 10) brings out this structure much more clearly than was expected. Under the microscope the octahedral structure is less obvious, owing to the granulation of the kamacite and the breaking up of the lines of taenite, which shows as bright specks. A few small nodules of troilite are present.

The faint circular line shown in the photograph (fig. 9) had not been previously noticed on the specimen, and it was at first thought to be due to a fault in the photograph (suggesting that a bottle had been placed on the wet film). But at a certain inclination of the light it is plainly seen on the etched surface of the meteorite. The parallel surface

<sup>1</sup> G. Tschermak, *Lehrbuch der Mineralogie*. 4th edit., Wien, 1894, p. 585.

If the slice and the surface at the edge were then smoothed and etched to see if the ring extended through the mass, but no indication of it could be detected. No explanation can be offered for this peculiar structure.

During this second etching, which proceeded slowly with very dilute acid, it was noticed that the faint Widmanstetter figures at first produced showed none of the granulation. They were sharper and more distinct, but the kamacite bars showed crenulated edges. As the etching proceeded the granular structure became evident and then more and more pronounced, while the octahedral structure became less and less distinct.

In its fine octahedral structure and percentage of nickel (p. 34) this Kamkas mass agrees with the various Gibeon masses; and a similar granulation is seen in one portion of the Mukerop mass. It is therefore probably a mass of the Gibeon shower that had been transported. The transportation by ox wagon of the 'Bethany' and Lion River masses evidently became too irksome, and they were abandoned north of the Orange River, to be found again and later continue their journey to Cape Town. The Kamkas mass was found a hundred miles north-west of the Gibeon farm area on a direct line to the seaport of Walfish Bay, with 170 miles still to go, and was then no doubt abandoned.

The granulation was no doubt effected by a moderate heat-treatment during a period previous to the entry of the mass into the earth's atmosphere. This was not intense enough to obliterate the octahedral structure; nor was it prolonged enough for the crystallization of coarser grains, as in the case of the Murnpeowie siderite.<sup>1</sup> The heat-treatment was also less intense than in a portion of the Mukerop mass, described by Brezina and Cohen and by Berwerth (*loc. cit.*). In the etched slices of the Mukerop mass one of the twinned portions shows a fine granulation, having at first sight the appearance of an ataxite, but in an oblique strong illumination some traces of a Widmanstetter structure are seen with a magnifying glass. Across the straight sharp line of contact the Widmanstetter structure in the adjacent portion of the twin is perfectly clear and not affected. How one portion of the twin could undergo a heat-treatment and the other escape is difficult to understand.

Chemical analyses of these two specimens have been made by Miss Ida Bennett in the Mineral Department of the British Museum. Her results given under I and II are in agreement with each other and with

<sup>1</sup> L. J. Spencer, Murnpeowie (South Australia), a granular type of meteoric iron. *Min. Mag.*, 1935, vol. 24, pp. 13-20, 3 pls., 1 text-fig.

previously published analyses (III-VII) of the Gibeon irons. The early determination by Sir John Herschel in 1838 of Ni 4.61 %, stated to be a hasty preliminary examination, is obviously too low; and C. U. Shepard's determination of Ni 6.70 % is also rather too low for a fine octahedrite.

TABLE I. Chemical analyses of meteoritic irons of the Gibeon shower.

|              | Fe.  | Ni.  | Co.   | Cu.  | Cr.  | C. | S.    | P.    | Cl.   | Insol. | Total. | Sp. gr. |
|--------------|------|------|-------|------|------|----|-------|-------|-------|--------|--------|---------|
| I. 92-38     | 7.68 | 0.30 | 0.006 | —    | —    | —  | nil   | 0.05  | —     | 0.03   | 100.45 | —       |
| II. 91-63    | 7.93 | 0.55 | 0.008 | —    | —    | —  | nil   | 0.04  | —     | 0.01   | 100.17 | —       |
| III. (93-30) | 6.70 | nil  | —     | —    | —    | —  | trace | trace | —     | —      | 100.00 | 7.45    |
| IV. 92-06    | 7.79 | 0.69 | 0.03  | 0.01 | —    | —  | 0.10  | 0.05  | —     | —      | 100.73 | —       |
| V. 91-07     | 8.18 | 0.63 | 0.03  | 0.02 | 0.01 | —  | 0.04  | 0.06  | trace | —      | 100.04 | 7.841   |
| VI. 90-96    | 8.19 | 0.46 | 0.04  | 0.02 | 0.02 | —  | trace | 0.18  | 0.01  | 0.01   | 99.89  | —       |
| VII. (91-37) | 7.97 | 0.50 | 0.02  | 0.04 | 0.05 | —  | 0.02  | 0.03  | n.d.  | —      | 100.00 | 7.783   |

- I. Kameelhaar farm. Analyst, Miss Hilda Bennett, 1941, on 1.87 grams.
- II. Kamkas farm. Analyst, Miss Hilda Bennett, 1941, on 2.35 grams.
- III. Lion River. Analyst, C. U. Shepard, loc. cit., 1853. Also Sn, K?, traces.
- IV. Lion River. Analyst, O. Sjöström in E. Cohen, *Meteoriten-Studien*. V. Ann. Naturhist. Hofmus. Wien, 1897, vol. 12, p. 43. Later addition of figures for Cu and S by J. Fahrenheit in E. Cohen, *Mitt. Naturwiss. Ver. Neu-Vorpommern und Rügen*, Berlin, 1901, vol. 32 (for 1900), p. 23; E. Cohen, *Meteoritenkunde*, 1905, Heft 3, p. 330.
- V. Bethany. Analyst, J. Fahrenheit in E. Cohen, loc. cit., 1900; *Meteoritenkunde*. Stuttgart, 1905, Heft 3, p. 335.
- VI. Mukerop farm. Analyst, O. Hildebrand in A. Brezina and E. Cohen, loc. cit., 1902; E. Cohen, *Meteoritenkunde*, 1905, Heft 3, p. 338.
- VII. Mukerop farm. Analyst, Krupp's chemical laboratory in A. Brezina and E. Cohen, 1902; E. Cohen, *Meteoritenkunde*, 1905, Heft 3, p. 338.

South-West Africa is noted for its meteorites. Besides the remarkable Gibeon shower, it has the largest of all known meteorites. This is the 60-ton Hoba<sup>1</sup> mass in Damaraland, about 400 miles north of Gibeon in Great Namaqualand. It is, however, of quite a different type, being a nickel-rich ataxite containing about 17 % of nickel.

<sup>1</sup> L. J. Spencer, Hoba (South-West Africa), the largest known meteorite. *Min. Mag.*, 1932, vol. 23, pp. 1-18, 1 pl., 5 text-figs.

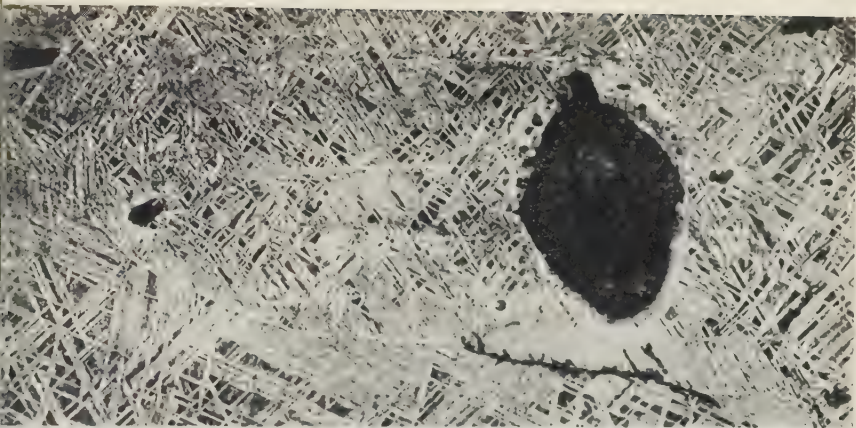


Fig. 8.

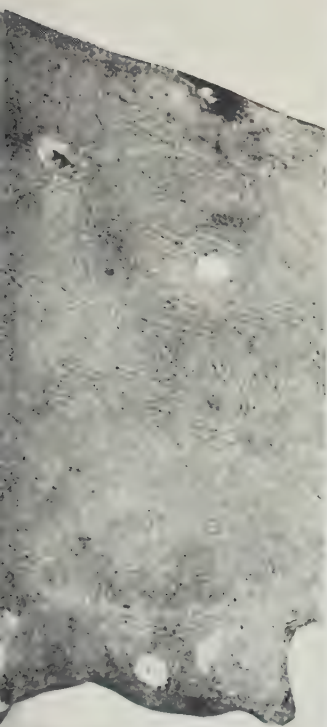


Fig. 9.

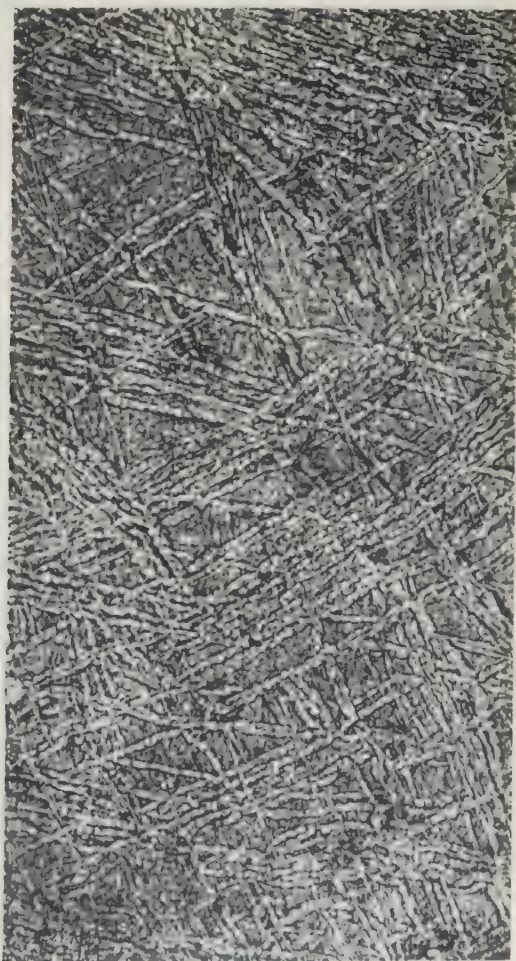


Fig. 10.



## EXPLANATION OF PLATES I AND II.

Polished and etched sections of meteoritic irons from the Gibeon shower, South-West Africa.

(Photographs by M. G. Sawyers, British Museum of Natural History.)

FIGS. 1-7 in the text.

PLATE I, FIG. 8. Kameelhaar farm, Gibeon. Portion of British Museum no. 1941,1, showing two crystal individuals with different orientation of the Widmanstetter figures. One large and several smaller nodules of troilite. Natural size.

FIG. 9. Kamkas farm, Maltahöhe. Portion of B.M. 1941,2, showing indistinctly the fine octahedral structure obscured by granulation. Patches covering small nodules of troilite. Natural size.

FIG. 10. Kamkas farm, Maltahöhe. Portion of fig. 9. Fine octahedral structure with granulation. The photograph, taken at a particular inclination of the light, comes out much better than was expected.  $\times 3$ .

PLATE II, FIG. 11. Kameelhaar farm, Gibeon. Portion of pl. I, fig. 8.  $\times 3$ .

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*Osbornite, meteoritic titanium nitride.*

By F. A. BANNISTER, M.A.

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[Read January 23, 1941.]

NEVIL STORY-MASKELYNE described in 1870 the mineral constituents of the Bustee meteorite, which was observed to fall in 1852 near Bustee about 45 miles west of Goruckpur, India.<sup>1</sup> The stone, weighing 1429 grams, now preserved in the British Museum collections, was found to consist chiefly of enstatite and diopside, and two constituents proved to be new minerals. Pale, chestnut-brown spherules of calcium sulphide, CaS, Story-Maskelyne named oldhamite<sup>2</sup> and golden-yellow octahedra found embedded chiefly in the oldhamite he named osbornite. One side of the meteorite has been ground to reveal the nodules of oldhamite and a coloured lithograph in W. Flight's book 'A chapter in the history of meteorites' reproduces the appearance of the chief mineral constituents very well.<sup>3</sup> The minute octahedra of osbornite are easily visible with a lens in the meteorite itself.

Two chemical analyses of oldhamite, involving the solution of nearly a gram of that mineral in hydrochloric acid, left a residue of only 28 milligrams of the osbornite crystals, an amount too small in those days for a complete chemical analysis. Qualitative tests, however, seemed to have convinced Story-Maskelyne and Flight that osbornite contained calcium, sulphur, and titanium or zirconium, and they drew the rather odd conclusion that perhaps it was an oxysulphide of calcium, titanium, and/or zirconium. Story-Maskelyne was using the microscope for separating out the components of coarsely crushed meteorites, then a novel procedure, and sometimes yielding only very small samples of any one constituent for subsequent study. The manipulation of a few tiny crystals and minute precipitates seventy years ago was no mean achieve-

<sup>1</sup> N. Story-Maskelyne, Phil. Trans. Roy. Soc. London, 1870, vol. 160, p. 189; Proc. Roy. Soc. London, 1870, vol. 18, p. 146.

<sup>2</sup> N. Story-Maskelyne, Rep. Brit. Assoc. Adv. Sci., 1863, for 1862 (32nd meeting, Cambridge), Trans. of Sections, p. 190. Preliminary note on the Bustee meteorite, with the first mention of the name oldhamite.

<sup>3</sup> W. Flight, London, 1887, p. 118; reprinted from Geol. Mag. London, 1875, dec. 2, vol. 2, p. 408, plate facing p. 401.

ment and mistakes were bound to occur. Probably Story-Maskelyne was not at all satisfied with his results for osbornite, but fortunately he refrained from using further material so rare and limited in supply. Since then osbornite has not been reported from any other meteorite and there can be only a minute amount in the Bustee stone itself.

In view of the difficulties which attended micro-chemical work in 1870 it would be unwise to show how the qualitative data published by Story-Maskelyne could have been differently interpreted. He did, however, publish two figures, the initial weight of osbornite analysed, viz. 28 milligrams and the weight 0.8 milligram of barium sulphate precipitated by barium chloride from the sublimate resulting from heating the crystals in a stream of chlorine. These figures correspond to only 4 % of sulphur so that sulphur can scarcely be one of the chief elements present. The same remark applies to calcium whether combined as sulphide or oxysulphide.

Story-Maskelyne had no difficulty in establishing the true symmetry of osbornite. He measured the interfacial angles of several crystals and found them all to be regular octahedra. It seemed to me probable that if the symmetry were cubic then an X-ray photograph might give additional information, perhaps a simple clue to the chemistry of the mineral. A crystal measuring 1/10 mm. across was picked out from one of the oldhamite spherules and rotated about an octahedral edge. The patterns obtained from this and another crystal rotated about a [111] axis revealed that osbornite has a cubic face-centred lattice with cell-edge 4.235Å. On consulting tabulated cell-edges of cubic substances<sup>1</sup> it seemed likely that artificial titanium 'cyanonitride' with rock-salt structure and cell-edge 4.24Å. should yield the same type of X-ray photograph as osbornite. This was readily confirmed by photographing several specimens of so-called titanium 'cyanonitride' in the British Museum collections. This compound is found in slags and bears from blast furnaces either singly or in groups of sharp copper-coloured cubes up to several millimetres across in a matrix of green slag often with abundant graphite. Both osbornite and the titanium 'cyanonitride' have a metallic lustre and excepting the darker colour of the latter certainly show a marked resemblance as well as yielding closely similar X-ray patterns. Flight<sup>2</sup> himself knew of the existence and appearance of titanium 'cyanonitride' and it was unfortunate that his

<sup>1</sup> I. E. Knaggs and B. Karlik, Tables of cubic crystal structure of elements and compounds. London, 1932, p. 30. [M.A. 5-171.]

<sup>2</sup> Footnote on p. 120 of his book, but not in Geol. Mag. (loc. cit.).

own qualitative tests suggested zirconium rather than titanium as a constituent of osbornite.

Entirely satisfactory confirmation of the presence of titanium in osbornite was obtained by further X-ray and qualitative chemical tests. Titanium 'cyanonitride' is known to change to titanium dioxide when heated in air.<sup>1</sup> A crystal fragment of titanium 'cyanonitride' was first heated to about 850° C. The sharp cube edges and corners were found to be rounded after this treatment. Under the microscope the original cube faces were seen to be polycrystalline and the X-ray photograph showed that the compound had altered to oriented rutile. A crystal of osbornite was subjected to the same treatment. The tiny octahedron also lost its sharp edges and developed polycrystalline surfaces. Moreover, the metallic lustre and golden colour were replaced by a translucent pale yellow appearance. This altered crystal yielded a rutile pattern and when crushed in methylene iodide gave birefringent fragments with no trace of any other component. The specific gravity of the rutile pseudomorph is 4.10, very close to the lowest values for rutile, 4.123, given in L. J. Spencer's tables.<sup>2</sup> The X-ray pattern, specific gravity, and microscopic tests of the rutile pseudomorph after osbornite show that titanium is the chief metal present in the original mineral. Dr. M. H. Hey produced some equally convincing colour reactions for titanium from four crystals of osbornite and has further shown that neither calcium nor sulphur can be detected. It is not unlikely that both these elements found by Flight were due to contamination of the osbornite with a very small amount of oldhamite.

Since there is insufficient osbornite available for a complete chemical analysis, Dr. Hey hopes later to make an approximate micro-chemical analysis. In the absence of a direct determination of nitrogen and carbon the cell-edge measurement and colour identify osbornite almost certainly with titanium nitride. The identification depends upon a considerable amount of previous work which has been carried out upon titanium 'cyanonitride' and the two end-members of the series titanium nitride-titanium carbide, to which it belongs.

W. H. Wollaston,<sup>3</sup> in 1823, published some interesting data on crystals from the slag of iron works at Merthyr Tydfil. He described them as cubes like pyrite with the lustre of burnished copper, specific gravity 5.3, which scratched quartz and possessed a high electrical conductivity.

<sup>1</sup> F. Wöhler, *Annalen der Chemie und Pharmacie*, 1850, vol. 73, p. 34.

<sup>2</sup> L. J. Spencer, *Min. Mag.*, 1927, vol. 21, pp. 356 and 364.

<sup>3</sup> W. H. Wollaston, *Phil. Trans. Roy. Soc. London*, 1823, p. 17.

He was probably the first to recognize the metallic-like properties of the substance and for that reason he wrongly identified it as metallic titanium. F. Wöhler (1850, loc. cit.) first analysed similar material from a blast furnace in the Harz Mountains, and found that intimate intergrowth with graphite made complete separation from the latter difficult. His analysis in table I gives the content of carbon in titanium 'cyanonitride' as 3.64 % and he is responsible for the formula  $\text{Ti}_5\text{CN}_4$  generally found in the literature. E. A. Rudge and F. Arnall<sup>1</sup> separated similar material from slag from a blast furnace converting Spanish haematite ore to pig-iron. They took especial care to free the titanium 'cyanonitride' from graphite by powdering finely in an agate mortar, passing through a 120-mesh sieve, then treatment with HCl to remove iron and HF to remove  $\text{SiO}_2$ , after which the bulk of the graphite was removed by flotation in a heavy liquid of specific gravity 3. In this way they found that the carbon content was up to 1 % (see table I), whereas clean crystals of the 'cyanonitride' visibly free of graphite gave carbon contents up to 3.4 %. V. M. Goldschmidt<sup>2</sup> published the first X-ray measurements on titanium 'cyanonitride' (Wöhler's material) and showed that the substance possesses the rock-salt type of crystal-structure. This material gave the cell-edge dimension  $4.243\text{\AA}$ . Four specimens of titanium 'cyanonitride' from various blast-furnace slags now preserved in the British Museum collections have been X-rayed with a view to determining whether there is any appreciable variation in cell-edge dimensions. Three of the four specimens have a cell edge  $4.24\text{\AA}$ . and one gave  $4.23\text{\AA}$ . Since the error due to film shrinkage, &c. is approximately  $\pm 0.01\text{\AA}$ , within these limits it can be said that specimens of titanium 'cyanonitride' from different slags have the same unit-cell dimensions.

Specimens of artificial titanium nitride and titanium carbide have also been photographed and give cell-edge values close to those reported by previous workers (tables II and III). The titanium nitride specimen prepared by A. E. van Arkel's method,<sup>3</sup> in which titanium chloride and nitrogen interact and form a deposit on a thin tungsten filament, is a pale-golden polycrystalline rod  $\frac{1}{2}$  mm. in diameter giving  $a$   $4.23\text{\AA}$ ., whereas a sample of black minutely crystalline titanium carbide gives  $a$   $4.31\text{\AA}$ . It is probable, therefore, from Rudge and Arnall's work and

<sup>1</sup> E. A. Rudge and F. Arnall, Journ. Soc. Chem. Industry, Trans., 1928, vol. 47, p. 376.

<sup>2</sup> V. M. Goldschmidt, Nachrichten Gesell. Wiss. Göttingen, Math.-Physikal. Kl., 1927, p. 390.

<sup>3</sup> A. E. van Arkel and J. H. de Boer, Zeits. Anorg. Chem., 1925, vol. 148, p. 345.

TABLE I. Chemical analyses of titanium 'cyanonitride', &amp;c.

|           |     | 1.      | 1a.   | 2.   | 2a.   | 3.    | 4.     | 4a.   | 5.    |
|-----------|-----|---------|-------|------|-------|-------|--------|-------|-------|
| Ti        | ... | 77.26   | 1.613 | 76.7 | 1.602 | 77.36 | 76.864 | 1.605 | 78.54 |
| N         | ... | 18.30   | 1.307 | 22.4 | 1.599 | 22.64 | 10.545 | 0.753 | 11.49 |
| C         | ... | 3.64    | 0.303 | 1.0  | 0.083 | —     | 9.741  | 0.812 | 9.97  |
| Graphite  | ... | 0.92    | —     | —    | —     | —     | 1.550  | —     | —     |
| Cell edge | ... | 4.243Å. | —     | —    | —     | —     | 4.27Å. | —     | —     |

1. Titanium 'cyanonitride' from an 80-lb. bear from a furnace in Rübeland, Harz Mts. F. Wöhler, 1850. Total 100.12.
- 1a. Calculated atomic proportions of no. 1. Molecular proportions of N and C add to 1.610 close to the titanium figure. This does not suggest that any graphite has been determined as combined carbon.
2. Titanium 'cyanonitride' = titanium nitride, from a blast furnace. E. A. Rudge and F. Arnall, 1928. Total 100.2, including Fe, Ca, Mg, 0.1.
- 2a. Calculated atomic proportions of no. 2, suggesting that either the nitrogen content is too high or that the carbon figure still includes graphite.
3. Theoretical composition of titanium nitride, TiN.
4. Cochranite = titanium carbonitride from Cleveland iron works. J. E. Stead, 1918. Total 98.927, including Fe 0.200, S 0.027, and Mn, Si traces.
- 4a. Calculated atomic proportions of no. 4, which suggest a deficit in N or C or both.
5. Theoretical composition of  $Ti_2CN$ .

from the X-ray measurements that titanium 'cyanonitride' is very close to pure titanium nitride and that although the carbon content may vary from one specimen to another it is not greater than 1 %.

Titanium nitride occurs not only in the slags and bears from blast furnaces, but has also been found in residues from acid solution of pig-iron and ferro-manganese. T. W. Hogg<sup>1</sup> described cubes and octahedra between 25 and 250 $\mu$  in size present in ferro-manganese and pointed out that although 1 c.c. of the metal contained about half a million crystals the maximum percentage by weight of the titanium compound was only 0.032. His description, however, does not provide any evidence for the existence of mixed crystals or solid solutions between titanium nitride and carbide. W. Hofmann and A. Schrader<sup>2</sup> who separated steel-grey cubes of titanium carbide from cast-iron bearing 5.1 % Ti noted particularly that they had not obtained a mixed carbide-nitride of titanium.

It is of some interest, therefore, that a re-examination of J. E. Stead's<sup>3</sup> cochranite, now preserved in the British Museum collections,

<sup>1</sup> T. W. Hogg, Rep. Brit. Assoc. Adv. Sci., 1894, for 1893 (63rd meeting, Nottingham), p. 721.

<sup>2</sup> W. Hofmann and A. Schrader, Archiv für das Eisenhüttenwesen, 1936, vol. 10, p. 65. (See table II for their X-ray data.)

<sup>3</sup> J. E. Stead, Journ. Iron and Steel Inst. London, 1918, vol. 97, p. 171. Min. Mag. 1919, vol. 18, p. 376. [M.A. 1-231.]

TABLE II. Cell-edge measurements of titanium nitride and carbide.

|                        | 1.   | 2.   | 3.    | 4.   | 5.    | 6.    | 7.    | 8.           |
|------------------------|------|------|-------|------|-------|-------|-------|--------------|
| TiN ...                | 4.40 | 4.23 | —     | —    | —     | —     | 4.225 | 4.23         |
| Ti(N,C) ...            | —    | —    | 4.243 | —    | —     | —     | —     | 4.23 to 4.24 |
| Ti <sub>2</sub> CN ... | —    | —    | —     | —    | —     | —     | —     | 4.27         |
| TiC ...                | 4.60 | 4.29 | —     | 4.31 | 4.311 | 4.320 | 4.315 | 4.31         |

1. K. Becker and F. Ebert, *Zeits. Physik*, 1925, vol. 31, p. 268; their values are too high.
2. A. E. van Arkel, *Physica*, Eindhoven, 1924, vol. 4, p. 286.
3. V. M. Goldschmidt, 1927; F. Wöhler's titanium 'cyanonitride' (loc. cit.).
4. L. R. Brantley, *Zeits. Krist.*, 1931, vol. 77, p. 505. [M.A. 5-22.]
5. M. von Schwarz and O. Summa, *Zeits. Elektrochem.*, 1932, vol. 38, p. 743.
6. W. G. Burgers and J. C. M. Basart, *Zeits. Anorg. Chem.*, 1934, vol. 216, p. 209.
7. W. Hofmann and A. Schrader, 1936 (loc. cit.). They give 4.325Å. for TiC separated from cast-iron.
8. F. A. Bannister, 1941. Osbornite 4.235Å.

TABLE III. Physical data for Osbornite, TiN, TiC, &amp;c.

|                        | Osbornite.    | TiN.          | Ti(N,C).  | Ti <sub>2</sub> CN. | TiC.          |
|------------------------|---------------|---------------|-----------|---------------------|---------------|
| Cell-edge <i>a</i> ... | 4.235         | 4.23          | 4.23-4.24 | 4.27                | 4.31Å.        |
| Colour ...             | golden-yellow | golden-yellow | copper    | blue                | black         |
| Hardness ...           | —             | 8-9           | 8-8.5     | >7                  | 9-10          |
| Melting-point          | —             | 3200° C.      | —         | —                   | 3400-3500° C. |
| Sp. gr. (calc.)        | 5.37          | 5.39          | 5.32*     | 5.14                | 4.93          |

\* Calculated by V. M. Goldschmidt from the cell-edge and Wöhler's chemical analysis, the unit cell containing 4Ti(N,C).

together with his chemical analysis shows that under certain conditions a product is formed in blast-furnace bears that lies almost exactly midway between TiN and TiC. He first gives an interesting account of the mode of formation of a furnace bear 'sometimes called an old horse, a sow or salamander', terms used for the mass of metal, sometimes weighing from 50 to 800 tons, which is found below the hearth level of a blast furnace after the furnace has been blown out. Then follows a detailed account of the crystalline products found in bears from the Cleveland works. Cochranite was detected in a polished section of a mass from one of the furnaces. Dark-blue cubes up to 50μ across embedded in a matrix of iron associated with graphite and manganese sulphide were separated for chemical analysis (table I). Although Stead assigned a wrong formula, calling it titanium dicyanide, his analysis shows that the blue cubes of cochranite must have a composition approximating to Ti<sub>2</sub>CN. He mentions that his carbon figure may include a little associated graphite. Hence the blue crystals should be

called titanium carbonitride. The crystals when crushed yield a dark blue powder which gives an X-ray photograph of the same pattern as titanium nitride and titanium carbide and a cell edge of  $4.27\text{\AA}$ . This measurement is confirmed by a single crystal photograph about a cube edge so that Stead's cochranite appears to be a uniform product. It would not be difficult to detect by X-ray measurements the existence of other mixed crystals in the series  $\text{TiN}-\text{TiC}$ , since the difference in the cell edges of the two end-members is  $0.08\text{\AA}$ . So far no evidence exists that a complete series of mixed crystals is afforded by material from slags, bears, or cast metal.

This review of work on products related to osbornite together with the chemical and X-ray data collected in tables I, II, and III concludes the evidence for its probable identity with titanium nitride. I have also confirmed the identity of oldhamite with calcium sulphide and of the diopside and enstatite with the corresponding terrestrial minerals. X-ray photographs have been taken of specimens of all three minerals originally separated from the Bustee meteorite by Maskelyne and Flight. The cell edge of oldhamite  $5.69\text{\AA}$ , is close to that of artificially prepared calcium sulphide  $5.686\text{\AA}$ , measured by I. Oftedal.<sup>1</sup> Moreover, the nodules of oldhamite, measuring up to 4 mm. across, are single crystals showing cubic cleavage and are probably bigger than any yet found in meteorites or produced artificially. The X-ray identification of the enstatite and diopside calls for no comment. It should be noted, however, that Maskelyne used the mineral name augite for the Bustee diopside containing only  $0.78\%$  iron oxide in the sense that we now use the name pyroxene.

The number of known titanium minerals is small. G. von Hevesy<sup>2</sup> states that the earth's crust contains  $0.63\%$  Ti chiefly as rutile and ilmenite. The titanium content of the earth, including the core, he gives as  $0.15\%$ , a little less than the average figure of  $0.19\%$  for stony meteorites, but considerably greater than the content of  $0.04\%$  for meteoritic irons. The occurrence of osbornite rather than rutile in the Bustee meteorite is in keeping with what little is known of the origin of meteorites but it is none the less a geochemical curiosity.

In conclusion, the formation of oriented rutile pseudomorphs after titanium nitride by oxidation (see page 38) merits attention as an interesting reaction in the solid state. Crystals not greater than  $\frac{1}{2}$  mm. across change to rutile throughout in an hour at bright red-heat.

<sup>1</sup> I. Oftedal, *Zeits. Physikal. Chem.*, 1927, vol. 128, p. 154.

<sup>2</sup> G. von Hevesy, *Journ. Chem. Soc. London*, 1931, p. 1. [*M. A.* 4-514.]

Crushing the pseudomorph reveals no central core of titanium nitride, and as previously mentioned an octahedron of osbornite yields a pseudomorph of specific gravity 4.10. It is remarkable that the change from a single crystal of titanium nitride (melting-point  $3200^{\circ}\text{C}.$ )<sup>1</sup> to that of polycrystalline rutile (melting-point  $1640^{\circ}\text{C}.$ )<sup>2</sup> should take place at a temperature certainly lower than  $1000^{\circ}\text{C}.$  The expansion factor for this change is 1.64, so that the final specific gravity 4.10, although 3-4 % below for rutile, suggests that the reaction proceeded accompanied by expansion without the formation of large holes or gas-filled cavities. The orientation of the rutile crystallites on the pseudomorph is not unexpected in view of the close relationship between the titanium atom lattices of TiN and rutile. It was first of all noticed on the X-ray photograph of the rutile pseudomorph after osbornite. Accurate setting of the tiny, rounded octahedron after oxidation about an axis of the original crystal was not achieved, and no detailed study of the photograph for that reason has been attempted. A small cube of titanium 'cyanonitride' also loses its sharp edges during oxidation, but I found it relatively easy to set up along a cube edge after heating. The larger polycrystalline cube faces gave a general glitter in reflected light which proved most useful for setting purposes. The X-ray photograph of this pseudomorph showed at once that the (110) faces of the rutile crystallites fell nearly parallel to the cube faces. This is consistent with the obvious probability that the *c*-axes of the rutile crystallites (*a* 4.59, *c* 2.95 Å.) would fall along the cube diagonals of the crystal of TiN, *a* 4.23 Å. ( $4.23/\sqrt{2} = 2.99$ ). This would also involve the superposition of the [110] axes of rutile and TiN, not so good a fit.

It is quite simple to calculate the positions of diffraction spots to be expected from the rotation of a rutile crystal about an axis inclined  $45^{\circ}$  to [001] and with two of its (110) faces vertical.<sup>3</sup> Diffractions contributed from the two horizontal cube faces of the rutile pseudomorph must also be considered. These would be relatively weak diffractions due to the rotation of rutile about the [110] axis. The X-ray photograph actually obtained gave streaks which agreed fairly well with the theoretical photograph to be expected on the basis of the assumed orientation of the rutile crystallites. The spread of the streaks along the curves of constant  $\theta$  (one-half the Bragg angle) may be due

<sup>1</sup> E. Friederich, *Zeits. Physik*, 1925, vol. 31, p. 813.

<sup>2</sup> O. Ruff, *Zeits. Anorg. Chem.*, 1913, vol. 82, p. 373.

<sup>3</sup> J. D. Bernal, *Proc. Roy. Soc. London, Ser. A.*, 1926, vol. 113, p. 117.  
[M.A. 3-333.]

to imperfection in the orientation and also to mis-setting the pseudomorph after its optically perfect cube faces were replaced by polycrystalline rutile. An attempt was made to increase the size of the rutile crystals by prolonged heating in a crucible over a Meker burner. It was not possible, however, to resolve the crystallites under the microscope sufficiently well to study the orientation over cube edges and corners, neither could I confirm Wöhler's description of sharp 'quadr-octahedra' with strong cross-stripping of the faces, a description which, incidentally, led him to think that they were anatase.

My thanks are due to Dr. M. H. Hey who carried out the qualitative micro-chemical tests on osbornite and to the Director of the Research Laboratories of the General Electric Company, Wembley, who provided the specimen of artificially prepared titanium nitride.

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*Metasomatism in the basalt of Haddenrig quarry near Kelso and the veining of the rocks exposed there.*

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[Read March 13, 1941.]

I. PETROLOGY AND CHEMISTRY OF THE ROCKS.

**H**ADDENRIG (Haddon Rig) quarry is situated three miles east of Kelso in Roxburghshire, near the road from Kelso to Mindrum in Northumberland. The rock quarried is marked on the Geological Survey Map (Scotland, Sheet 26) as a basalt intrusive into the Lower Carboniferous lavas (Kelso traps). The absence of exposed contacts excludes any direct field evidence of its intrusive character, but the appearance of the fresh basalt from the quarry suggests that it belongs to a sill or a plug, as it is in many ways similar to other intrusive basalts of the Kelso district. The evidence of the orientation of the felspar laths in the basalt is not entirely conclusive. With the exception of the northern part of the quarry where the orientation is vertical, elsewhere it is more or less horizontal. This suggests a sill. The vertical orientation of laths in the northern part of the quarry may be due either to the presence of a feeding channel or to eddies in the sill.

TABLE I. Modal composition of basalts (weight %).

|             |               |     |     | 1.    | 2.    |
|-------------|---------------|-----|-----|-------|-------|
| Phenocrysts | Olivine ...   | ... | ... | 2.30  | 4.10  |
|             | Felspar       | ... | ... | 1.85  | 20.65 |
|             | Pyroxene      | ... | ... | 2.10  | 5.10  |
| Groundmass  | Felspar       | ... | ... | 58.10 | 25.05 |
|             | Pyroxene      | ... | ... | 20.05 | 20.30 |
|             | Iron-ore      | ... | ... | 11.90 | 11.85 |
|             | Chlorite, &c. | ... | ... | 3.70  | 12.95 |

1. Fresh olivine-basalt (Dunsapie type).

2. Altered olivine-basalt (transition to metabasalt).

In the northern part of the quarry a perfectly fresh bluish-grey basalt is exposed (fig. 1). Although the phenocrysts are comparatively small and few in number this rock may be called olivine-basalt of Dunsapie

type (table I, no. 1). The olivine phenocrysts are partly serpentinized. The unaltered olivine appears to be a normal magnesia-rich type. The pyroxene phenocrysts have ragged edges and enclose small crystals of felspar and portions of the groundmass. The felspar phenocrysts are

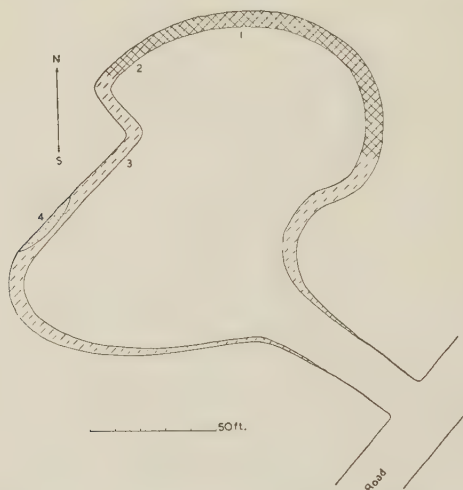


FIG. 1. Map of Haddenrig quarry. Basalt, cross-hatching; metabasalt, dashed lines, potash-spilite, stippling. The scale is approximate. 1-4, location of rocks analysed.

labradorite (table II, nos. 1, 2), while the groundmass laths are somewhat more alkaline (table II, nos. 3, 4, 5, 6). A small amount of interstitial alkali-felspar is also present, but analcime has not been detected. The pyroxene of the groundmass is a normal augite occurring in the form of small prismatic grains. Titanomagnetite, microfibrous chlorite, and apatite complete the groundmass. Occasionally small nests of amygdules are found surrounded by zones rich in pyrite. The amygdules are formed of chalybite which lines the walls of the cavity and calcite which infills the remaining space.

The chemical analysis of the fresh basalt (table III, no. 1) is very close to the average of Dalmeny-Dunsapie types of Carboniferous basalts (22, p. 62) although the alkalis are slightly above the average.

The olivine-basalt becomes progressively more alkaline in the southern direction. The plagioclase becomes distinctly albitized and dusty in appearance, but other constituents are not affected. The phenocrysts are increasing both in size and in number. An analysis of the albitized

basalt as given in table III (no. 2) shows an increase of alkalis and silica as compared with the fresh olivine-basalt.

Table II. Results of measurement of the feldspars on the Fedorov stage.

|     |                                                                             |        | Co-ordinates of the<br>plane of association. |         |          | Twin-law. | 2V.                                                       | An %.                                                   |
|-----|-----------------------------------------------------------------------------|--------|----------------------------------------------|---------|----------|-----------|-----------------------------------------------------------|---------------------------------------------------------|
|     |                                                                             |        | $\gamma$                                     | $\beta$ | $\alpha$ |           |                                                           |                                                         |
| 1.  | $\left\{ \begin{array}{l} a \\ b \end{array} \right.$                       | ... .. | 26                                           | 66      | 82       | Albite    | $\left\{ \begin{array}{l} +80 \\ +75 \end{array} \right.$ | $\left\{ \begin{array}{l} 49 \\ 50 \end{array} \right.$ |
| 2.  | $\left\{ \begin{array}{l} a \\ b \end{array} \right.$                       | ... .. | 29                                           | 63      | 80       | Carlsbad  | $\left\{ \begin{array}{l} +79 \\ +80 \end{array} \right.$ | $\left\{ \begin{array}{l} 54 \\ 52 \end{array} \right.$ |
| 3.  | (Zonal method)                                                              |        | ...                                          | ...     | ...      | ...       | ...                                                       | 42                                                      |
| 4.  |                                                                             |        | ...                                          | ...     | ...      | ...       | ...                                                       | 45                                                      |
| 5.  |                                                                             |        | ...                                          | ...     | ...      | ...       | ...                                                       | 39                                                      |
| 6.  |                                                                             |        | ...                                          | ...     | ...      | ...       | ...                                                       | 41                                                      |
| 7.  | $\left\{ \begin{array}{l} a \\ b \end{array} \right.$                       | ... .. | 27                                           | 65      | 80       | Albite    | $\left\{ \begin{array}{l} +86 \\ +82 \end{array} \right.$ | $\left\{ \begin{array}{l} 51 \\ 59 \end{array} \right.$ |
| 8.  | $\left\{ \begin{array}{l} a \\ b \end{array} \right.$                       | ... .. | 22                                           | 68      | 87       | Albite    | $\left\{ \begin{array}{l} +86 \\ +86 \end{array} \right.$ | $\left\{ \begin{array}{l} 40 \\ 35 \end{array} \right.$ |
| 9.  | ...                                                                         | ...    | 6                                            | 86      | 87       | Albite    | -88                                                       | 25                                                      |
| 10. | ...                                                                         | ...    | 0                                            | 90      | 90       | —         | -8                                                        | Sanidine                                                |
| 11. | ...                                                                         | ...    | 0                                            | 90      | 90       | —         | -72                                                       | Orthoclase                                              |
| 12. | $\left\{ \begin{array}{l} \text{inner} \\ \text{outer} \end{array} \right.$ | ... .. | 0                                            | 90      | 90       | Carlsbad  | -70                                                       | Orthoclase                                              |
|     | $\left\{ \begin{array}{l} \text{inner} \\ \text{outer} \end{array} \right.$ | ... .. | 26                                           | 65      | 80       | Albite    | +78                                                       | 50                                                      |
| 13. | $\left\{ \begin{array}{l} \text{inner} \\ \text{outer} \end{array} \right.$ | ... .. | 5                                            | 87      | 86       | —         | -52                                                       | Anorthoclase                                            |
|     | $\left\{ \begin{array}{l} \text{inner} \\ \text{outer} \end{array} \right.$ | ... .. | 33                                           | 63      | 72       | —         | +80                                                       | 65                                                      |

1, 2, phenocrysts in olivine-basalt; 3-6, groundmass laths in olivine-basalt; 7-13, phenocrysts in potash-spilite.

$a$  and  $b$  refer to two adjoining twin-individuals; the plane of association in all cases is (010).

The albitized basalt gradually passes southwards and upwards into a highly altered greenish-grey rock which may be called metabasalt. A rock transitional between basalt and metabasalt as measured on the Shand stage (table I, no. 2) shows a great increase in the amount of phenocrysts. The lower part of the metabasalt zone is equally rich in phenocrysts, but in the upper part of this zone the phenocrysts almost entirely disappear. In the metabasalt all the ferromagnesian minerals are transformed into chlorite, the feldspar is greatly albitized, and the iron-ore is partly altered into leucoxene. The carbonates are abundant, not in vesicles, but in ragged patches replacing other minerals. An analysis of a non-porphyrific variety of metabasalt (table III, no. 3) shows a very high amount of combined water and a relatively low amount of alkalis. This analysis is not quite representative of the metabasalt zone as a whole. The inclusion of the porphyritic (feldspar-

rich) fraction of metabasalt would no doubt raise the amount of alkalis and lower that of water.

TABLE III. Analyses of rocks from Haddenrig quarry and other rocks for comparison.

|                                   | 1.    | 2.     | 3.    | 4.    | 5.     | 6.    | 7.     | 8.    | 9.     | 10.    |
|-----------------------------------|-------|--------|-------|-------|--------|-------|--------|-------|--------|--------|
| SiO <sub>2</sub> ..               | 46.96 | 48.52  | 46.22 | 47.95 | 47.03  | 37.73 | 44.65  | 37.30 | 47.03  | 39.72  |
| TiO <sub>2</sub> ..               | 2.51  | 2.76   | 2.32  | 2.58  | n.d.   | 2.38  | 1.91   | 2.70  | 1.89   | 0.90   |
| Al <sub>2</sub> O <sub>3</sub> .. | 14.68 | 13.86  | 15.52 | 15.82 | 22.45  | 16.49 | 14.18  | 14.79 | 17.78  | 12.37  |
| Fe <sub>2</sub> O <sub>3</sub> .. | 4.96  | 3.47   | 2.57  | 1.44  | 7.00   | 5.14  | 7.21   | 7.14  | 7.48   | 2.52   |
| FeO ..                            | 8.18  | 9.28   | 9.37  | 2.56  |        | 6.70  | 8.50   | 7.08  | 4.20   | 0.91   |
| MnO ..                            | 0.23  | 0.12   | 0.06  | 0.03  | n.d.   | 0.09  | 0.05   | trace | —      | —      |
| MgO ..                            | 6.26  | 5.06   | 6.02  | 3.64  | 8.79   | 7.96  | 6.31   | 8.13  | 3.19   | 5.82   |
| CaO ..                            | 8.61  | 8.02   | 5.54  | 8.09  | 2.92   | 7.85  | 6.72   | 6.70  | 10.61  | 12.57  |
| Na <sub>2</sub> O ..              | 3.62  | 4.36   | 2.54  | 3.23  | 2.63   | 0.95  | 2.22   | 2.20  | 3.82   | 0.64   |
| K <sub>2</sub> O ..               | 0.90  | 1.29   | 0.85  | 5.24  | 4.55   | 1.41  | 1.81   | 2.56  | 0.80   | 4.18   |
| P <sub>2</sub> O <sub>5</sub> ..  | 0.51  | 0.54   | 0.72  | 0.93  | n.d.   | 0.27  | 0.28   | 0.34  | 0.40   | 0.49   |
| FeS <sub>2</sub> ..               | —     | —      | —     | —     | —      | 0.06  | trace  | trace | 0.35   | 0.29   |
| CO <sub>2</sub> ..                | 0.03  | 0.06   | 1.60  | 6.98  | 1.90   | 3.21  | 1.98   | 3.60  | 0.59   | 16.42  |
| H <sub>2</sub> O+ ..              | 1.81  | 2.22   | 5.78  | 1.42  | 3.65   | 7.01  | 3.49   | 5.20  | 2.15   | 3.30   |
| H <sub>2</sub> O— ..              | 0.49  | 0.60   | 0.84  | nil   | —      | 2.23  | 0.82   | 2.20  | —      | —      |
|                                   | 99.75 | 100.16 | 99.95 | 99.91 | 100.92 | 99.48 | 100.13 | 99.94 | 100.29 | 100.13 |
| Sp. gr. ..                        | 2.924 | 2.867  | 2.755 | 2.666 | —      | —     | —      | —     | —      | —      |

1. Olivine-basalt (Dunsapie type), Haddenrig quarry. Anal. S. I. Tomkeieff.
2. Olivine-basalt (Dunsapie type, albitized), Haddenrig quarry. Anal. F. Herdsman.
3. Metabasalt, Haddenrig quarry. Anal. F. Herdsman.
4. Potash-spilite, Haddenrig quarry. Anal. F. Herdsman.
5. Potash-spilite, lava, Knot Law, Millers Dale, Derbyshire. Anal. H. C. Sargent (1917, p. 22).
6. Olivine-basalt (highly altered), lava, Tearsal farm, near Matlock, Derbyshire. Anal. S. I. Tomkeieff (new analysis).
7. Olivine-basalt (Dalmeny type), lava (lower part), Cottonshope, Northumberland. Anal. S. I. Tomkeieff (1931, p. 266). In the previously published analysis of this rock H<sub>2</sub>O— was erroneously given as 1.98.
8. Olivine-basalt (Dalmeny type, altered), same locality, upper part of the lava flow. Anal. F. Herdsman (new analysis).
9. Olivine-basalt (Markle type), Carlekemp, North Berwick. Anal. T. C. Day (1928).
10. Vesicular silicified and carbonated basalt. Eel Burn, North Berwick. Anal. T. C. Day (1928).

In the eastern part of the quarry horizontal schlieren from one to six inches in thickness are found in the metabasalt. On both sides they show a continuous, although sharp, transition into a fine-grained metabasalt. They are made of a very coarse dolerite-pegmatite with large patches of chloritic mesostasis. Large albitized felspar crystals and large chloritized pyroxene crystals project inwardly from the margins into the centre of the bands. The schlieren probably represent portions of highly hydrous magma drawn out during the intrusion. Another interesting feature of this rock is the presence of angular fragments of quartz rock. These are of frequent occurrence in the western part of the quarry and it may be that they are not confined to the metabasalt,

although none was found in the other parts of the quarry. These fragments vary in size from minute particles to platy inclusions a couple of inches across. They consist entirely of mosaic quartz and could justifiably be called quartzite. Each fragment is surrounded by a reaction rim of granular or vermicular pyroxene now altered to chlorite and this suggests that they are foreign inclusions. Inclusions of sedimentary material are frequently found in the Scottish Carboniferous lavas and intrusions. Day, for example, has described fragments of sandstone altered to quartzite enclosed in basalt at Upper Whitfield (8). The strata below the lavas into which the basalt complex of Haddenrig is intruded belongs to the upper Old Red Sandstone and it may be that the quartzite inclusions are the metamorphosed flaggy sandstone of this formation.

In the western part of the quarry a mass of light greenish-grey rock is exposed in the upper part of the quarry cutting. The exposed rock mass is approximately thirty feet long and ten feet in thickness and it fills a hollow in the metabasalt. The upper part of it and the surrounding metabasalt were probably removed by denudation. The transition between this rock and the metabasalt is rapid but continuous. Externally this rock looks like a trachyte and the first impression gained by microscopical examination is that of a highly altered carbonatized trachyte. It is a porphyritic rock, but unless the felspar phenocrysts are completely chloritized they are not clearly visible in the hand-specimen.

The feldspars in this rock are greatly alkalinized, carbonatized, and chloritized. As a rule only a few relics of the original lime-plagioclase can be seen. The majority of phenocrysts are completely transformed into an alkali-feldspar, but in the partly altered lime-plagioclase phenocrysts the alkali-feldspar occurs in ragged patches and stringers. Quite frequently only the outer border of the original plagioclase is preserved. The replacing feldspar has sometimes the appearance of perthite with albite and orthoclase patches and stringers.

Seven phenocrysts from this rock were measured on the Fedorov stage and the results of these measurements are given in table II. Nos. 7 and 8 probably represent the original unaltered or slightly altered plagioclase. No. 9 is composed of oligoclase with stringers of orthoclase, the whole resembling a perthite. No. 10 shows a very small optic axial angle and must be a sanidine. In this case the measurements were repeated several times to avoid any mistake. More phenocrysts of this type were noted. The presence of sanidine suggests a comparatively high temperature at which the replacement took place. No. 11

represents the commonest type of replacement felspar which is orthoclase. No. 12 is a plagioclase partly replaced by orthoclase. No. 13 shows that the replacing felspar is anorthoclase. Some phenocrysts are completely replaced by carbonate and chlorite.

There is only a faint indication of the former presence of olivine or pyroxene phenocrysts. The groundmass consists of highly altered and turbid felspar laths, chlorite, carbonate, iron-ore, and leucoxene.

The chemical analysis of this rock (table III, no. 4) shows high amounts of potash and carbon dioxide and comparatively low amounts of iron oxides and magnesia. This is in perfect agreement with the microscopical evidence, e.g. the abundance of potash-felspar and carbonates. The chemical analysis may be interpreted as that of a basalt enriched in potash and carbon dioxide, but the mineralogical composition of this rock is far removed from that of basalt. This rock may in certain respects be compared with marloesite described by H. H. Thomas, with the keratophyre-spilite described by E. Lehmann, with the trachybasalt described by T. C. Day (10), and finally with spilite. The non-carbonate portion of the rock in its chemical composition (table IV) has a resemblance to a variety of åkerite described by Brögger under the name of hurumite (4, p. 71), but hurumite has a different mineralogical composition.

In my opinion the best name for this rock is potash-spilite. Some petrologists will at once object to this name on the ground that the name spilite ought to refer only to soda-rich rocks. All this depends on the connotation of a rock name. The name spilite (meaning spotted) was proposed by Brongniart in 1827 (5, p. 98) and he applied it to amygdaloidal calcite-rich rocks of basaltic composition. It was in this sense that the term was used until in 1911 Dewey and Flett (11) added another character to the definition, namely richness in soda which manifested itself in the abundance of albite or oligoclase in the rock. Strange to say, this additional character became the dominant one to the exclusion of the original character as defined by Brongniart. Meanwhile Sargent in 1917 described certain carbonate- and potash-rich basaltic lavas from Derbyshire under the name of potash-spilite (18). These rocks are similar to other spilites except that they have more potash than soda, and in my opinion they are true spilites. A new name is unnecessary when it is possible to extend the connotation of the existing term spilite. Thus extended the definition of spilite is as follows: a carbonate-rich rock of basic composition and often amygdaloidal, with alkali-felspar (usually, but not always, soda-rich), pyroxene

(usually chloritized), and sometimes olivine (in small amounts and serpentinized). According to this definition the carbonate-rich rock from Haddenrig quarry is a potash-spilite.

The Haddenrig intrusive complex consists therefore of several rock facies showing a perfect gradual transition from one to the other. Above is the potash-spilite, then metabasalt, then albitized basalt, and finally normal olivine-basalt. As comparison of chemical analyses is rather difficult in the case of altered rocks two attempts have been made to recalculate them—the first on the basis of equal volumes of rocks (table IV, nos. 1-4) where the figures of each analysis are multiplied by the quotient—specific gravity altered rock/specific gravity fresh rock. The second is a recalculation of the analyses omitting the carbonates (table IV, nos. 1a-4a). The analyses recalculated to the equal volumes of rocks is probably the best way of comparing the composition of the different members of a rock series.

TABLE IV. Analyses (table III) recalculated to equal volumes of rocks (nos. 1-4); the same without the carbonates (1a-4a); A, hurumite (Brögger, 1931, p. 71).

|                                |    | 1.    | 2.    | 3.    | 4.    | 1a.    | 2a.    | 3a.    | 4a.    | A.    |
|--------------------------------|----|-------|-------|-------|-------|--------|--------|--------|--------|-------|
| SiO <sub>2</sub>               | .. | 46.96 | 47.57 | 43.50 | 43.65 | 47.11  | 48.52  | 48.12  | 57.26  | 59.85 |
| TiO <sub>2</sub>               | .. | 2.51  | 2.70  | 2.18  | 2.35  | 2.52   | 2.76   | 2.47   | 3.08   | 1.61  |
| Al <sub>2</sub> O <sub>3</sub> | .. | 14.68 | 13.59 | 14.60 | 14.43 | 14.70  | 13.86  | 16.19  | 18.90  | 15.88 |
| Fe <sub>2</sub> O <sub>3</sub> | .. | 4.96  | 3.40  | 2.42  | 1.31  | 4.97   | 3.47   | 2.68   | 1.72   | 0.19  |
| FeO                            | .. | 8.18  | 9.10  | 8.82  | 2.33  | 8.21   | 9.21   | 7.97   | 0.31   | 5.94  |
| MnO                            | .. | 0.23  | 0.12  | 0.06  | 0.03  | 0.23   | 0.12   | 0.06   | 0.04   | 0.09  |
| MgO                            | .. | 6.26  | 4.96  | 5.66  | 3.32  | 6.28   | 5.06   | 6.25   | 3.52   | 2.15  |
| CaO                            | .. | 8.61  | 7.85  | 5.21  | 7.37  | 8.64   | 7.99   | 5.07   | 2.26   | 4.46  |
| Na <sub>2</sub> O              | .. | 3.62  | 4.27  | 2.39  | 2.94  | 3.63   | 4.36   | 2.65   | 3.86   | 2.87  |
| K <sub>2</sub> O               | .. | 0.90  | 1.26  | 0.80  | 4.78  | 0.90   | 1.29   | 0.89   | 6.25   | 5.95  |
| P <sub>2</sub> O <sub>5</sub>  | .. | 0.51  | 0.53  | 0.68  | 0.85  | 0.51   | 0.54   | 0.75   | 1.11   | 0.04  |
| H <sub>2</sub> O               | .. | 0.03  | 0.06  | 1.51  | 6.37  | —      | —      | —      | —      | —     |
| H <sub>2</sub> O +             | .. | 1.81  | 2.18  | 5.25  | 1.29  | 1.81   | 2.22   | 6.03   | 1.69   | 0.95  |
| H <sub>2</sub> O -             | .. | 0.49  | 0.59  | 0.79  | —     | 0.49   | 0.60   | 0.87   | —      | —     |
|                                |    | 99.75 | 98.18 | 93.87 | 91.02 | 100.00 | 100.00 | 100.00 | 100.00 | 99.98 |

In the series of Haddenrig the most significant is the variation of soda, potash, water, and carbon dioxide. This is illustrated on fig. 2 which is drawn on the basis of table IV (nos. 1-4). Soda reaches its maximum in the zone of albitized basalt, water in the zone of metabasalt, and potash and carbon dioxide in the zone of potash-spilite. This suggests that these compounds have diffused through the magma at a different rate, and of the two alkalis potash has overtaken soda.

Potash diffusion, in contrast to soda diffusion, is not a well-studied process. The majority of igneous rocks give rise to soda-rich differen-

tiates and contact adinoles testify to the penetrative power of soda. Here are a few recorded facts demonstrating the diffusion of potash. In her brilliant study of the transfusion of quartzite Miss D. L. Rey-

nolds (16) has shown that potash is highly diffusible. In her analyses the potash index

$$(K_2O \times 100 : K_2O + Na_2O)$$

of hornblendite (original magma) is 39, while that of syenite (transfused quartzite) is 51. Brögger in his study of the essexites of Oslo district (4) gives three analyses of essexites from Randvikholmen in which the potash index of the central part of the intrusion is 33 and that of the margin 44, while the potash index of hurumite, which according to Brögger is a differentiation product of essexite, is 67. In the case of the Eel Burn basalt described by Day (9) the potash index of the fresh basalt is 17 and that of the metasomatized basalt 87. It is also interesting to note that in the Fen district (4) the potash index of the melteigite-urtite series is 28, while in the differentiation products of this magma it rises steadily—in the kâsenite-söbite series to 90

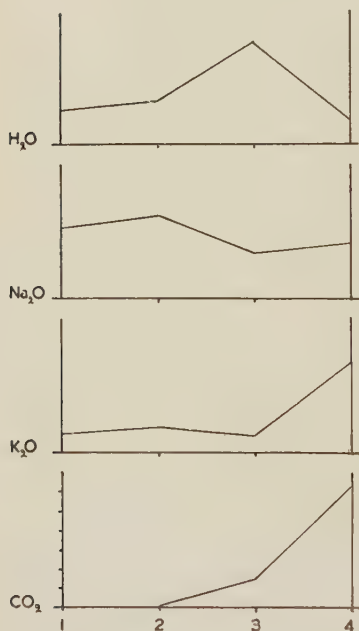


Fig. 2. Variation diagram for H<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, and CO<sub>2</sub> in olivine-basalt (1), albitized basalt (2), metabasalt (3), and potash-spilite (4).

and in the damkjernite-rauhaugite series to 60.

The majority of the British Carboniferous igneous rocks are soda-rich, but occasionally one finds among them potash-rich facies, like those described by Day (9) and Sargent (18). Some years ago while working on the igneous rocks of Derbyshire I analysed a highly altered lava from the Matlock district. This analysis, hitherto unpublished, is given in table III (no. 6). Strictly speaking, the rock analysed cannot be called spilite, but the analysis shows a higher amount of potash than soda. Another example may be drawn from Northumberland. An analysis of the lower part of a Carboniferous lava flow from Cottons-hope was published by me in a previous paper (21). A new analysis

of the upper part of the same flow shows a marked increase in potash (table III, nos. 7 and 8).

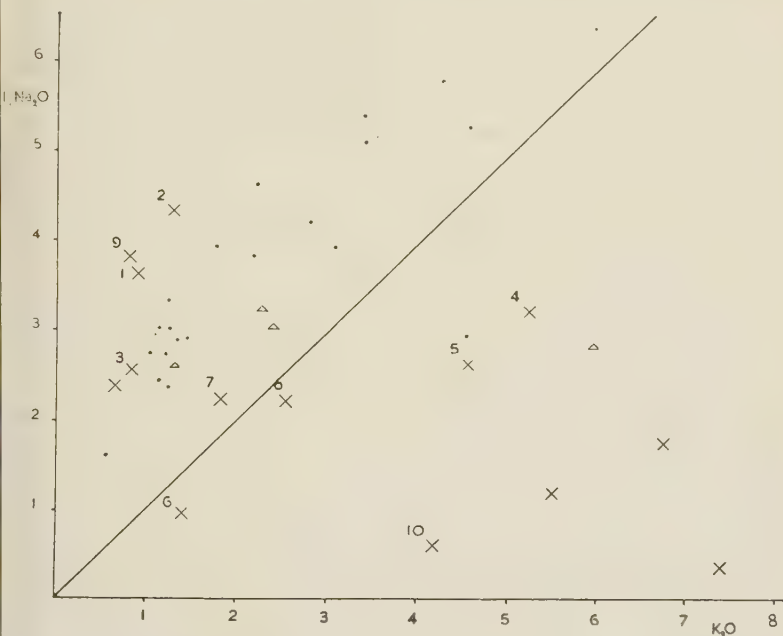


FIG. 3. Na<sub>2</sub>O-K<sub>2</sub>O diagram. The averages for various types of British Carboniferous-Permian igneous rocks are represented by dots; the analyses of Haddenrig rocks and other rocks given for comparison (table III) are represented by crosses; the unnumbered crosses represent other analyses of spilites from Derbyshire as given by H. C. Sargent; the triangles represent the essexite-hurumite series as given by W. C. Brögger.

A clear idea of the relation between soda and potash in the Carboniferous igneous rocks may be derived from fig. 3. With the exception of rhyolite all the averages of the principal rock types (22, p. 62) fall in the soda-rich region. The analyses of Haddenrig basalt and metabasalt are also situated in the same region, while that of Haddenrig potash-spilite as well as the potash-spilites from Derbyshire fall in the potash-rich region of the diagram. On the same diagram Brögger's essexite-hurumite series is represented by triangles. In the majority of cases the enrichment in potash takes place without any reduction in soda, but in the case of the Eel Burn rocks (nos. 9 and 10) the sum of the alkalis remains more or less constant.

## II. THE VEIN ROCKS AND CARBONATES.

The complex of Haddenrig is penetrated by numerous vertical veins with an approximate strike NW.-SE. The veins vary from a fraction of an inch to six inches in thickness. The contacts with the surrounding rocks are sharp and as a rule each vein is fringed by a narrow contact zone of silicified or carbonatized rock. Three types of vein rocks may be distinguished:

(1) Carbonate veins. These are composed almost entirely of carbonates distributed in patches of unequal grain-size. Fragments of spilite and metabasalt are frequent. The cavities are infilled by quartz which seals up the carbonate rhombohedra.

(2) Carbonate-silica veins. These are composed of small corroded carbonate rhombohedra embedded in a quartzose groundmass. The poikilitic quartz grains usually show an undulose extinction or brush structure passing into flamboyant structure. This suggests a meta-colloidal nature of quartz.

(3) Quartz veins. These are frequently banded. The bands vary from 0.5 to 3 mm. in thickness and are composed of coarse and fine quartz grains, chalcedony, and finely fibrous and flamboyant quartz. Small amounts of carbonate, chlorite, prehnite, and gouge clay are also found in these veins.

The cross-cutting relations of these veins show that their order of formation was as follows: carbonate, carbonate-silica, and finally quartz veins.

The fine-grained nature of the carbonates made impossible a mechanical separation of the minerals and the carbonates of the rocks and veins were therefore analysed in bulk. In each case  $\text{CO}_2$  was determined in a separate portion. The finely ground material was treated by hot dilute  $\text{HCl}$ ; and  $\text{CaO}$ ,  $\text{MgO}$ , and the sesquioxides were determined in the usual way.  $\text{MnO}$  was in all cases present in minute quantities and was not determined. It was found that the amount of  $\text{CO}_2$  was never sufficient to satisfy the amounts of the determined oxides and that the most soluble mineral other than the carbonate was the iron-ore. It was decided, therefore, to calculate all  $\text{CaO}$  and  $\text{MgO}$  as carbonates and the remaining  $\text{CO}_2$  to allot to  $\text{FeO}$ . The results of these approximate analyses are given in table V. When placed in the order: fresh rock—altered rock—early veins—late veins, the analyses show a steady increase of  $\text{CaCO}_3$  and decrease of  $\text{FeCO}_3$ , while  $\text{MgCO}_3$  remains small. Charlewood, in his review of vein carbonates (7), suggested grouping

Table V. Composition of the carbonates in rocks and veins.

|                                | CaCO <sub>3</sub> . | MgCO <sub>3</sub> . | FeCO <sub>3</sub> . | % carbonate<br>in the rock. |
|--------------------------------|---------------------|---------------------|---------------------|-----------------------------|
| Olivine-basalt (albitized) ... | 26.20               | 0.65                | 73.15               | 0.16                        |
| Metabasalt ... ..              | 30.15               | 1.50                | 68.35               | 4.01                        |
| Potash-spilite ... ..          | 68.50               | 8.45                | 23.05               | 16.13                       |
| Carbonate-silica vein ...      | 76.15               | 3.75                | 20.10               | 46.90                       |
| Quartz vein ... ..             | 85.50               | 0.50                | 14.00               | 1.50                        |

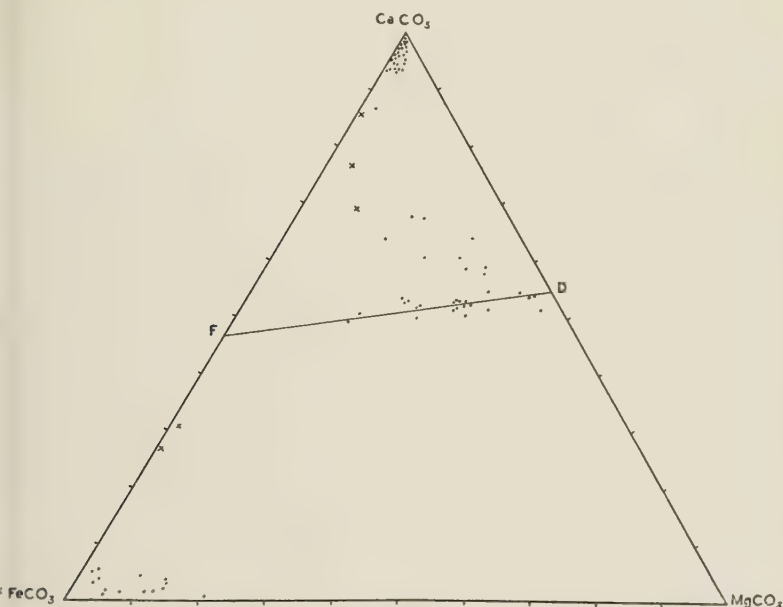


FIG. 4. Triangular diagram representing the composition of 78 analyses of carbonates from veins. The analyses of carbonates from the Haddenrig rocks and veins are represented by crosses. F = ferrodolomite, D = dolomite.

them, in three groups according to their degree of occurrence in veins. Calcite, ankerite, ferrodolomite, and dolomite are frequently found, chalybite is less common, while magnesite and rhodochrosite are rare. According to Hawkes and Smythe (14) ankerite represents an isomorphous mixture of dolomite ( $\text{MgCO}_3 \cdot \text{CaCO}_3$ ) and ferrodolomite ( $\text{FeCO}_3 \cdot \text{CaCO}_3$ ) and that it may hold up to 20 %  $\text{CaCO}_3$  in solid solution. I have recalculated 78 analyses of vein carbonates collected from various sources in terms of three components,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FeCO}_3$  (+  $\text{MnCO}_3$ ), and have made a plot of them on a triangular diagram (fig. 4). This diagram suggests the abundance of calcite, chalybite, dolomite, and

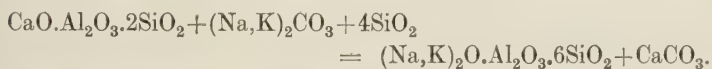
ankerite. Magnesite was not recorded, probably because it is found only in veins associated with ultrabasic intrusions, which I did not collect. The analyses of the carbonates from the rocks and veins of Haddenrig are marked by crosses on the diagram. They probably represent mixtures of chalybite and calcite. Basalt and metabasalt are apparently richer in chalybite, while spilite and the vein rocks are richer in calcite. One may infer from this that chalybite, as being the less soluble of the two, was formed at a higher temperature and near the source, and that calcite was deposited farther away from the source at lower temperature.

### III. CONCLUSIONS.

The magmatic complex of Haddenrig presents a fine example of metasomatism within a single rock mass. The gradual transition from basalt to metabasalt and from metabasalt to potash-spilite suggests a process of endomorphic metasomatism being responsible for these changes. Processes of this kind have been called autolysis, protopneumatolysis, autopneumatolysis, and autometamorphism. There is, however, no direct evidence as to the nature of the agent of metasomatism. It is difficult to identify it either as liquid or as gas, or to name the process itself—hydrothermal or pneumatolytic. It is almost certain that this process took place during the later stages of the consolidation of the magma and that the agents of metasomatism attacked already formed minerals, such as calcic-plagioclase and pyroxene. The results of this metasomatism are: the alkalization of feldspar, the chloritization of pyroxene, and the carbonate replacement of all minerals. This suggests that the principal agents of metasomatism were the alkalis, water, and carbon dioxide. The alkalization of calcic-plagioclase also requires additional silica and this means that silica must also have been present. The unused portions of the carbonates and of silica were probably precipitated in the veins. Were the agents of metasomatism juvenile or resurgent, or, in other words, did they belong to the magma itself or were they derived from some assimilated sediments? Although it is true that quartzitic xenoliths are found in the metabasalt, there is, apart from this, no indication whatever that the magma has assimilated sediments. If we compare analyses of basalt and potash-spilite we can see no evidence of assimilation of either calcareous or siliceous sediments. The difference between the composition of the two rocks lies mainly in the amounts of  $K_2O$  and  $CO_2$  and this cannot be explained by addition of sedimentary material. The Scottish Carboni-

ferous igneous rocks are relatively rich in carbon dioxide. This is shown by the calculated average composition of basalt in which the amount of  $\text{CO}_2$  is 0.32 %. Considering that the majority of published analyses refer to compact fresh rocks and do not, as a rule, include carbonate-rich vesicular varieties, the actual amount of  $\text{CO}_2$  in the magma was probably many times greater. It is thought, therefore, that the agents of metasomatism of the Haddenrig magmatic complex were of juvenile origin.

The transfer of volatiles to the upper part of the magmatic body could not have been easily achieved during the later stages of the consolidation of the magma. This transfer took place probably through diffusion in a still liquid magma. Thus in the upper, volatile-rich zone of the magmatic body the early formed minerals—olivine, pyroxene, plagioclase, and iron-ore—were reacted upon by the hydrous alkali-carbonate-silicate residual solution or gas, and this gave rise to a series of late-magmatic or deuteric minerals such as alkali-felspar, chlorite, leucoxene, and carbonate. Calcic-plagioclase, for example, can be transformed into an alkali-felspar according to the equation:



This reaction has been successfully tested experimentally by Eskola, Vuoristo, and Rankama (12). The best presentation of the process of albitization (this applies to alkalinization in general) was given by Bailey and Grabham in the following words (1, p. 253):

‘We are thus led to suppose that the albitization was performed shortly after the consolidation of the ground-mass, and that the agency at work consisted of residual solutions. We may advance the hypothesis that in certain volcanic centres, e.g. Arthur’s Seat, some portions of the magma were discharged exceptionally rich in carbon dioxide (or some other unknown constituent); that during crystallization of the lava an unusual proportion of soda was thus retained in solution; and that the residual liquors then began to react with the minerals which had crystallized. Olivine was converted into serpentine and chlorite, while the most basic feldspars were replaced by albite. The process may be crudely expressed by saying that *the lava at this stage was stewing in a concentrated solution of sodium carbonate.*’

The comparison of analyses (tables III and IV; fig. 3) suggests that the rate of diffusion of potash was higher than that of soda. The nature of the agents of metasomatism can only be conjectured. Probably alkali carbonates, hydrous alkali silicates, and even alkali phosphates were active.

During recent years a number of works have been published dealing

with the deuteric alteration of rocks, soda, potash, and carbonate metasomatism, and hydrothermal veins. Here is a brief summary of some of them in chronological order.

Knopf (15) described a sericite-ankerite-albite-quartz-rock from the contact-zone of a greenstone. Gillson (13) described orthoclasization of plagioclase and quartz in the border phase of quartz-monzonite by means of ascending potash-bearing emanations. Singewald (20) described autometasomatism in monzonite-porphyry, the stages of alteration of which were: albitization, sericitization, and carbonatization. Butler (6) quite justifiably extended Bowen's reaction series to deuteric and hydrothermal formations. Ross (17) gave an illuminating picture of the late-magmatic processes linked up with vein formation. Bastin (2) explained the well-known 'red rock' of Pigeon Point as being due to hydrothermal alteration of the diabase. And, finally, Schwartz (19) gave a review of our knowledge of the hydrothermal alterations of igneous rocks.

Present-day petrologists are not solely interested in the normal igneous rocks. More and more they are becoming convinced that not only are the early magmatic stages important, but that an equal importance is attached to the late magmatic and even the post-magmatic stages.

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*Hydrozincite from Narlarla, West Kimberley district,  
Western Australia.*

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With a chemical analysis by MAURICE CRABTREE, B.Sc.

[Read January 23, 1941.]

HINTZE (1930) has pointed out the considerable variation in analyses of hydrozincite and the various formulae assigned to this mineral. Further data concerning this comparatively rare mineral are therefore desirable. Hydrozincite has been found at Narlarla, Western Australia, and this material is described below.

Narlarla is situated in the Napier Range, West Kimberley district (long.  $124^{\circ} 43' \text{ E.}$ , lat.  $17^{\circ} 16' \text{ S.}$ ), 75 miles due east from Derby, on the south side of the Barker River gorge (fig. 1). Several small silver-lead-zinc ore-deposits occur in the hills at Narlarla which are made up entirely of Devonian limestone. The occurrences have been described by Woodward (1907, p. 11), who, in his report, gives the results of assays of several specimens of the ore. These occurrences are unique as they are the only known post pre-Cambrian primary ore-deposits in Western Australia. (Secondary gold deposits occur in the Donnybrook sandstone which is considered to be probably of Permian age (Forman, 1936).) The unique character of the Narlarla deposits has been noted by Simpson (1939, p. 218), who, however, offers no explanation as to their genesis. The absence of any post-Devonian igneous intrusives, other than the leucite-lamproite plugs (Wade and Prider, 1940) which are intrusive into the Permian rocks of the Fitzroy River area to the south of Narlarla, seems to indicate that these deposits are genetically related to the lamproite magma. The nearest known occurrence of the leucite-lamproites is at Mt. North, some 15 miles to the south (fig. 1), but there may be closer occurrences as the area has not been very closely examined, and the widespread distribution of the lamproite magma has been demonstrated (Wade and Prider, 1940).

During a recent trip through the West Kimberley area in connexion with an examination of the leucitic volcanic rocks, I visited the northern lead ore-deposit in the Narlarla Hills and noted the presence, in con-

considerable amount, of a white to pale pink fibrous mineral which on later examination proved to be hydrozincite. This mineral has been analysed and is described below.

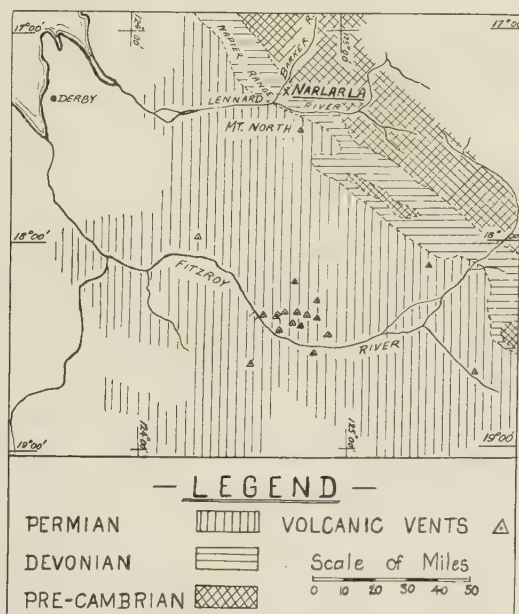


FIG. 1. Geological sketch-map of part of the West Kimberley district, showing the location of Narlarla with respect to the post-Permian volcanic vents.

The material collected came mostly from broken ore lying on the surface, and in these specimens the following minerals were noted: malena, blende, cerussite, hydrozincite, limonite, and very small amounts of malachite and chessylite. In a shallow shaft on the south-west side of the outcrop the ore consists largely of cerussite and limonite forming a flat band two feet thick, with bands six inches wide of greyish mudstone both above and below, separating the ore from the normal limestone country. This mudstone is spotted and veined with white hydrozincite. The richest hydrozincite specimens, however, came from broken ore fragments on the surface and the oxidized specimens obtained at Narlarla all contain from 30 to 40 % of hydrozincite segregated into regular areas up to  $\frac{1}{2}$  cm. across. These specimens are earthy lusted, spotted pink and white coloured, and have a drusy structure. The mudmass is earthy, fine-grained, pinkish in colour, and is composed

mainly of carbonate minerals (including zinc carbonate) and clayey material coloured with finely dispersed limonite. The druses, which form on the average approximately 40 % by volume of the rock, and which vary in size up to  $\frac{1}{2}$  cm. across, are lined and in most instances completely filled with white hydrozincite. In the larger druses the hydrozincite is seen to have a very pale pinkish colour and in several places it shows very slight staining by malachite or aurichalcite. Examination under the microscope shows that the hydrozincite occurs as thin water-clear plates, usually elongated and bounded by parallel faces. The plates all lie on the same face (100) and other orientations were only obtained with difficulty as the plates are exceedingly thin. Extinction on (100) is straight and the optic elongation positive. Interference-figures obtained on (100) were the characteristic 'flash figure', indicating that the optic axial plane is outside the field of view. No basal sections could be obtained (slices could not be cut as the minute separate crystals decompose on the slightest heating). Plates on edge, i.e. on (010), show extinction-angles  $\gamma : c$  to  $40^\circ$ . Some of the (100) plates were highly birefringent, others showed low grey interference-colours (due entirely to their extreme thinness). The refractive indices obtained on these plates by immersion in oils were  $\alpha$  1.635,  $\gamma'$  1.745.

Ford and Bradley (1916) on hydrozincite from Nevada stated that the optic axial plane and vibration-direction  $\gamma$  are apparently parallel to (100). Larson (1921, pp. 90, 267) on material from other localities gave  $\alpha = b$  and  $\gamma : c$  moderate, and in his second edition (1934, p. 194)  $\gamma : c$  as  $13^\circ$ . The properties of the Narlarla hydrozincite may be summarized as follows:

Colour: pale pink to white (transparent).

Habit: thin elongated monoclinic plates ((100) plates elongate parallel to  $c$ ).

Extinction straight on (100),  $\gamma : c = 40^\circ$  on (010).

Optical elongation positive.

Biaxial, optical sign unobtainable, optic axial plane normal to (010).

Refractive indices  $\alpha$  1.635,  $\gamma'$  1.745; birefringence  $\gamma' - \alpha$  0.110.

Does not fluoresce under ultra-violet light.

Blowpipe tests: in closed tube decrepitates and water evolved. The residue is bright golden-yellow when hot and pale sea-green when cold.

Soluble with effervescence in cold dilute acids.

Microchemical test for zinc with potassium mercuric thiocyanate gives characteristic feathery crosses with slight purplish colour due to the presence of copper

Material from the drusy cavities was analysed and the result is shown in table I. This material contained a very small amount of the limonitic clayey material of the groundmass of the rock and some cerussite. In

The calculation of the analysis  $\text{Fe}_2\text{O}_3$  has been calculated as limonite,  $\text{Al}_2\text{O}_3$  as allophane, and  $\text{PbO}$  as cerussite. Microchemical tests were made to determine whether any lead was in the hydrozincite. A sample such as that analysed was dissolved in 1:10  $\text{HNO}_3$ , evaporated to dryness, taken up with 0.5 % acetic acid, and tested with KI, yielding an abundance of yellow lead iodide. Some of the purest material from the larger druses was tested in a similar manner and only a slight reaction for lead obtained—this indicates that the hydrozincite itself contains little, if any, lead.

The portion recorded as 'insoluble' in the analysis was material insoluble in  $\text{HCl}$  and probably represents silica resulting from the decomposition of the clay mineral. The alumina has been calculated as allophane rather than as kaolin because: (1) it has gone into solution with  $\text{HCl}$ ; (2) there is only sufficient  $\text{SiO}_2$  to satisfy  $\text{Al}_2\text{O}_3$  in a 1:1 ratio; and (3) if it is calculated as kaolin then there is a considerable excess of negative ions over positive ions in the residue.

TABLE I. Analysis and calculation of hydrozincite from Narlarla.  
(Analyst, M. Crabtree.)

|                                             | %      | Mol. prop. | Limonite. | Allophane. | Cerussite. | Residue (hydrozincite). |
|---------------------------------------------|--------|------------|-----------|------------|------------|-------------------------|
| Insoluble ( $\text{SiO}_2$ )                | 1.15   | 0.0191     | —         | 0.0177     | —          | 0.0014                  |
| $\text{Al}_2\text{O}_3$ ...                 | 1.80   | 0.0177     | —         | 0.0177     | —          | —                       |
| $\text{Fe}_2\text{O}_3$ ...                 | 2.64   | 0.0165     | 0.0165    | —          | —          | —                       |
| $\text{CaO}$ ...                            | trace  | —          | —         | —          | —          | —                       |
| $\text{MgO}$ ...                            | 0.04   | 0.0010     | —         | —          | —          | 0.0010                  |
| $\text{PbO}$ ...                            | 3.96   | 0.0177     | —         | —          | 0.0177     | —                       |
| $\text{ZnO}$ ...                            | 62.10  | 0.7638     | —         | —          | —          | 0.7638                  |
| $\text{CuO}$ ...                            | 1.75   | 0.0220     | —         | —          | —          | 0.0220                  |
| $\text{CoO}$ ...                            | 0.09   | 0.0012     | —         | —          | —          | 0.0012                  |
| $\text{NiO}$ ...                            | 0.18   | 0.0024     | —         | —          | —          | 0.0024                  |
| $\text{FeO}$ ...                            | 15.19  | 0.3451     | —         | —          | 0.0177     | 0.3274                  |
| $\text{Fe}_2\text{O}_3$ ...                 | 0.01   | 0.0001     | —         | —          | —          | 0.0001                  |
| $\text{H}_2\text{O}^{+100^\circ \text{C.}}$ | 10.17  | 0.5648     | 0.0247    | 0.0885     | —          | 0.4516                  |
| $\text{H}_2\text{O}^{-100^\circ \text{C.}}$ | 0.96   | —          | —         | —          | —          | —                       |
|                                             | 100.04 |            |           |            |            |                         |

In the residue the ratio of anions to cations is 789:779, almost 1:1, and the ratio  $\text{CO}_2:\text{H}_2\text{O} = 327:452$ . This ratio lies closer to 3:4 than to 1:1, and the formula for the Narlarla hydrozincite therefore appears to be  $3\text{ZnCO}_3 \cdot 4\text{Zn}(\text{OH})_2$  with slight replacement of Zn by Cu, Ni, and Co. Hintze (1930, p. 3352) has pointed out the considerable variation in analyses of hydrozincite and the various formulae assigned to this mineral. Ford and Bradley (1916) and Perrier (1916) consider that hydrozincite has the formula  $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ . In a later paper by

Biehl (1919) an analysis of hydrozincite of unknown locality gave the formula  $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2$ . Larsen (1934, p. 194) lists hydrozincite as having the formula  $7\text{ZnO} \cdot 3\text{CO}_2 \cdot 4\text{H}_2\text{O}$ . The Narlarla mineral appears to be closer to the formula given by Larsen than to other suggested formulae.

Since the relative proportions of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are of the greatest importance in connexion with the formula of this mineral, it may be of interest to state the method by which these constituents were determined in the analysis quoted above. The  $(\text{H}_2\text{O}^+ + \text{CO}_2)$  was determined by loss on ignition on material dried at  $100^\circ \text{C}$ . The  $\text{CO}_2$  was estimated by treating a separate portion with  $\text{HCl}$  and absorption of  $\text{CO}_2$  in  $\text{Ba}(\text{OH})_2$ —the excess  $\text{Ba}(\text{OH})_2$  was neutralized with  $\text{HCl}$  using phenolphthalein and then the  $\text{BaCO}_3$  was titrated with  $\text{HNO}_3$  using methyl orange as an indicator. The  $\text{H}_2\text{O}^+$  was obtained by difference on these two results. It was unfortunate that absolutely pure material could not be obtained for this analysis—it contains some clayey material in which one cannot be certain of the actual amount of water. Judging from the ratio of anions to cations in the residue (table I) there should be slightly more water present in the residue—even if this be added to balance, the formula still lies closest to that suggested by Larsen.

*Summary.*—Hydrozincite from Narlarla is similar optically to that listed by Larsen with the exception that  $\gamma : c = 40^\circ$  ( $13^\circ$  according to Larsen). Its formula approaches most closely to  $3\text{ZnCO}_3 \cdot 4\text{Zn}(\text{OH})_2$  with slight replacement of Zn by Cu, Co, and Ni. The ore-deposit where this mineral has been noted is unique, being the only post pre-Cambrian primary ore-deposit known in Western Australia, and it is suggested that it is genetically related to the post-Permian lamproite magma of the Fitzroy River basin.

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